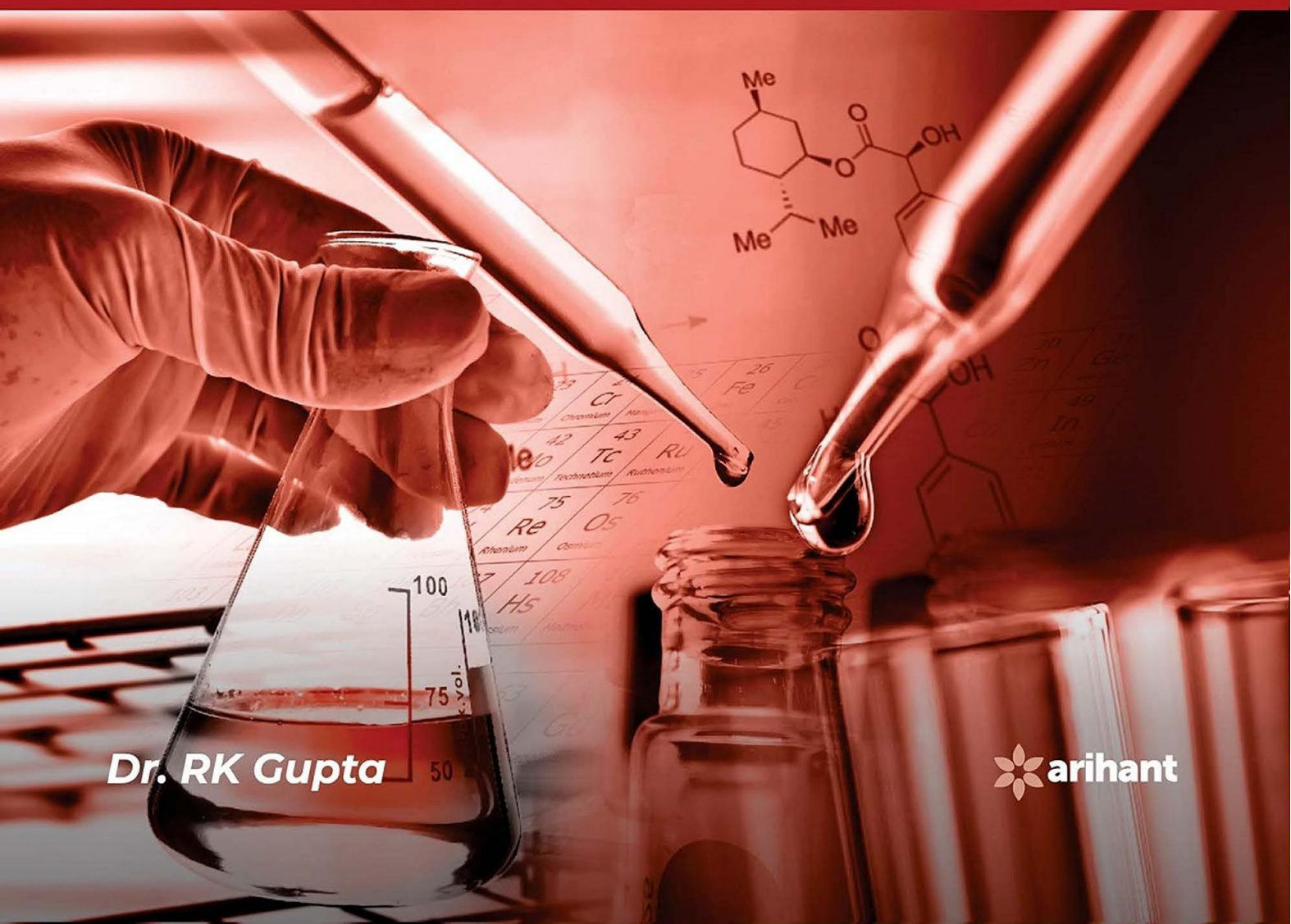


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# A TEXTBOOK OF INORGANIC CHEMISTRY

for JEE Main & Advanced



**Dr. RK Gupta**

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# **INORGANIC CHEMISTRY**

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**Dr. RK Gupta**



**ARIHANT PRAKASHAN (Series), MEERUT**





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# PREFACE

In the recent years, the format and pattern of JEE Main & Advanced have been constantly changing. In pursuance to these latest changes, I present a new text book the Inorganic Chemistry to help the students master the Inorganic Chemistry. The book covers all the aspects of Inorganic at the level of Classes XI-XII with a view to master the syllabus of all Engineering Entrances.

## *Features of the Book*

- Text has been devised in such a way as to be assimilable, without a prior knowledge of the Inorganic Chemistry.
- The basic thrust of the NCERT books has been followed and most of the problems from the NCERT books have been included in each chapter.
- The whole text has been divided into twenty chapters, out of which seven devoted to General section, the backbone of Chemistry from which almost 40% questions are being asked in JEE Main & Advanced every year.
- *p*-block elements have been sub-divided into six separate blocks to make it more relevant to NCERT pattern and examination oriented.
- Every chapter starts with Quick-Points that is the idea in nut-shell of the concepts/basics for application in the current unit and thus helpful in creating confidence among aspirants.
- Target-Exercises at the end of each Section are meant to check your ability at the spot before you proceed to the next Section. This is followed by Practice-Exercises on NCERT-based questions.
- There are lots of other exercises (with complete solutions) for testing analytical-skills. They include Comprehension-Based Questions, True-False, Fill-in-blanks, Assertion-Reason, Matrix-Matching, Integer Answer Types, MCQs with One and More than One Correct Options, Very Short and Analytical Questions compiled Sections-wise.
- Brain –Twisters are provide to sharp your knowledge specially of Olympiad Aspirants.
- Deep – Focus are scattered throughout the text. These are the warning concepts to catch your eyes for spot revision before examination.
- Essential Inorganic CHEMISTRY is thought to be non-conceptual, nevertheless, I hope this text will be able to debunk this misconception and will be immensely helpful.

## Acknowledgement

Finally, there are many faculty and students, who have helped in the development of contents by their valuable suggestions and unsolicited comments. They know who they are, and I hope that they will accept my sincere thanks for all they did.

It is also a pleasure to acknowledge the many people for their friendly assistance in completing this book, especially Shri Y C Jain, Chairman, Arihant for encouraging me at each step, and for being an exemplary Publisher, and good friend too. My special thanks are also to Daya Sindh Computers, Meerut for completing the book well in time. I am also indebted to MS Rawat, Keshav Agarwal, Harsh Kumar and Narendra Singh who left no stone unturned for completing this project successfully.

I must thank Almighty God for His inspiration and guidance, and my family members for their unquestioning timely encouragement without which this work would not be possible.

I would be glad to from the faculty and other of any errors which may have escaped. Any suggestion whereby the book can be improved will be heartily welcomed.

Dr. RK Gupta  
raghvesh@gmail.com

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Chemistry touches almost every aspect of our lives, our culture, and our environment. Its scope encompasses the air we breathe, the food we eat, the fluids we drink, our clothings, dwellings, transportation and fuel supplies, and our fellow creatures.

# Fundamental Concepts of Inorganic Chemistry

Chemistry is the science that describes matter—its chemical and physical properties, the chemical and physical changes it undergoes, and the energy changes that accompany those processes.

Matter includes everything that is tangible, from our bodies and the stuff of our everyday lives to the grandest objects in the universe. Some call chemistry as the central science. It rests on the foundations of mathematics and physics and in turn underlies the life sciences biology and medicine.

All living matter contains carbon combined with hydrogen. The chemistry of compounds of carbon and hydrogen is called **Organic Chemistry**. The study of substances that do not contain carbon combined with hydrogen is called the **Inorganic Chemistry**. The branch of chemistry that is concerned with the detection or identification of substances present in a sample (*qualitative analysis*) or with the amount of each that is present (*quantitative analysis*) is called **Analytical Chemistry**. **Physical Chemistry** applies the **mathematical theories** and methods of physics to the properties of matter and to the study of chemical processes and the accompanying energy changes. As its name suggests, **Biochemistry** is the study of the chemistry of processes in living organisms.

## Matter and Energy

**Matter** is anything that has mass and occupies space. Mass is a measure of the quantity of matter in a sample of any material. The more massive an object is, the more force is required to put it in the motion. All bodies consist of matter. Our senses of sight and touch usually tell us that an object occupies space. In the case of colourless, odourless, and tasteless gases (such as air), our senses may fail us.

### Learning Framework of the Chapter

- Matter and Energy
- Physical and Chemical Changes
- Laws of Chemical Combination
- Dalton and Constitution of Matter
- Atomic Number, Mass Number and Isotopes
- Equivalent Weight
- The Mole
- Per cent Composition and Empirical Formula

## 2 Essential Inorganic Chemistry

**Energy** is defined as the capacity to do work or to transfer heat. Energy can be in the form of

- (i) mechanical energy
- (ii) light energy
- (iii) electrical energy
- (iv) heat energy

Energy is classified into two principal types:

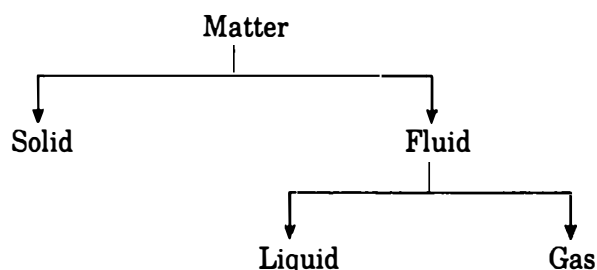
### Kinetic Energy

A body in motion, such as rolling boulder, possesses energy because of its motion. Such energy is called **kinetic energy**. It represents the capacity for doing work directly. It is easily transferred between objects.

### Potential Energy

It is the energy an object possesses because of its position, condition or composition. Coal, for example, possesses chemical energy, a form of potential energy, because of its composition. Thermal plants burn coal, producing heat which is converted to electrical energy. A boulder located at top of a mountain possesses potential energy because of its height. It can roll down the mountain side, and potential energy is converted into kinetic energy.

### Different States of Matter



A molecule is the smallest particle of any kind of matter, element or compound, which can exist in the free state and can still preserve the character of that kind of matter. **The properties of a substance**, are the properties of its molecules.

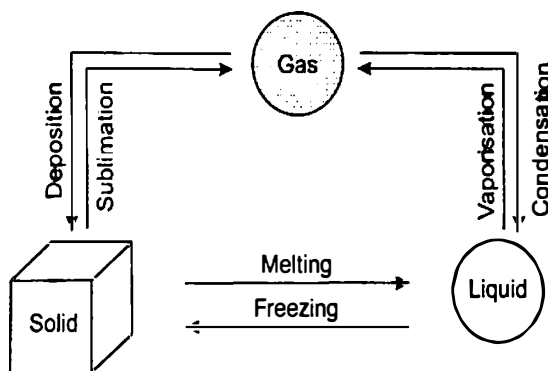


Fig. 1.1

### Solids

In the solid state, the intermolecular force is very strong. The molecules in a solid species, therefore, cling together, with a great force. Thus, solids have definite shape and volume.

### Liquid

In the liquid state, the intermolecular forces are very feeble. They are still perceptible. Thus, liquid has no definite shape but takes the shape of that part of the vessel in which it is stored.

### Gases

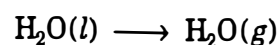
In the gaseous state, the intermolecular force is negligible and molecules lie far apart from one another. They move in different directions with different velocities colliding among themselves and against sides of the container.

| Properties           | Ice<br>(Solid H <sub>2</sub> O)   | Liquid H <sub>2</sub> O                                                      | Steam<br>(Gaseous H <sub>2</sub> O)                           |
|----------------------|-----------------------------------|------------------------------------------------------------------------------|---------------------------------------------------------------|
| Rigidity             | Rigid (definite shape and volume) | Flows and assumes shape of container (no definite shape but definite volume) | Fills any container completely (no definite volume and shape) |
| Expansion on heating | Slight                            | Slight                                                                       | Expands infinitely                                            |
| Compressibility      | Slight                            | Slight                                                                       | Easily                                                        |
| Melting point        | solid >                           | liquid >                                                                     | Compressed gas                                                |

We know that when water is boiled, it disappears; when a candle burns, both the wick and the wax entirely disappear, practically all its weight is lost. Again a piece of magnesium wire, on being strongly heated in air, burns with a brilliant light and leaves a white residue, which when weighed, will be found to be heavier than the piece of magnesium taken.

When we try to follow these, we are confronted with some questions which naturally come to our mind? Is water actually destroyed? Is there is destruction of the substance of which the candle is decomposed? Whence does the additional weight of magnesium come? Can matter be created? We can certainly answer these questions one by one.

- When water is boiled, it only changes its state and is not destroyed.



The candle loses weight due to combustion and the products are colourless gases that are disappearing into the atmosphere.

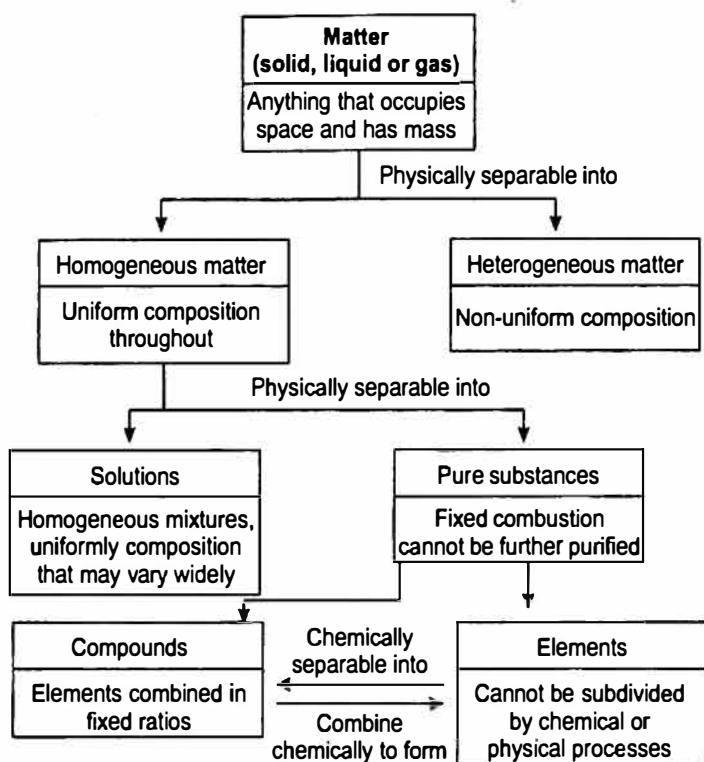


Fig.1.2 Classification of matter

Magnesium gains weight due to its reaction with the oxygen of the atmosphere and gives white residue (of magnesium oxide). But in no chemical action any kind of matter is destroyed or created.

## Physical and Chemical Changes

Matter is capable of undergoing variety of changes as

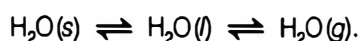
### Physical Change

If there is change in some of the specific properties like the state (solid to liquid or *vice-versa*), texture, electrical or magnetic without bringing about any change in the composition or constitution of its molecules, then this type of change is termed as physical change.

**Original state can be restored by change in experimental condition.**

#### Illustration :

$\text{H}_2\text{O}$  (liquid) is converted into  $\text{H}_2\text{O}$  vapour (steam) on heating, and steam into  $\text{H}_2\text{O}$  (liquid) on condensation.  $\text{H}_2\text{O}$  (liquid) is converted into ice at freezing point, and ice melts to  $\text{H}_2\text{O}$  (l) at melting point.



Thus, it is completely a physical change.

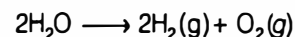
- When an electric current is passed into copper wire wrapped over iron, it is magnetised. When flow of electric current stops, magnetic behaviour is also lost. Thus, it is a physical change.

### Chemical Change

If there is change in the specific properties of the matter due to change in the composition or constitution of its molecules, this is termed as chemical change. **There is formation of new molecules as a result of a chemical change.**

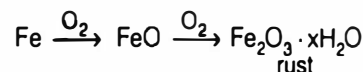
#### Illustration :

- Acidified water is converted into hydrogen and oxygen due to electric decomposition



This is a chemical change, since  $\text{H}_2\text{O}$  is converted into new compounds  $\text{H}_2$  and  $\text{O}_2$ .

- When iron piece is exposed to air for a long time, resulting takes place. Rust appears in the form of brown-coloured layer and is formed when iron reacts with moist air.



#### Think Yourself !

When a candle (of wax) burns, wax melts. After sometime wax is completely converted into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . What is the type of this change?

We know that wax is made of carbon, hydrogen and oxygen when wax melts, it is a **physical change**. But when it is converted into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  due to burning, it is a **chemical change**.

Table 1.1 Distinction between Physical and Chemical Change

|                | Physical change                                                                                                                                  | Chemical change                                                                                                                                           |
|----------------|--------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|
| Example        | $\text{H}_2\text{O(s)} \xrightleftharpoons[\text{f.p.}]{\text{m.p.}} \text{H}_2\text{O(l)}$                                                      | $\text{CaCO}_3(\text{s}) \xrightarrow{\text{Heat}} \text{CaO(s)} + \text{CO}_2(\text{g})$                                                                 |
| Composition    | no change, water in solid and liquid state have identical composition H and O being in 2 : 1 ratio                                               | Changes due to formation of new compounds. $\text{CaCO}_3(\text{s})$ , $\text{CaO(s)}$ and $\text{CO}_2(\text{g})$ have completely different composition. |
| Properties     | Physical properties differ but chemical properties are identical.                                                                                | Physical properties and chemical properties of the reactants and products are quite different.                                                            |
| Stability      | A temporary change, above equilibrium is reversible. Original state is restored by change in experimental condition.                             | A permanent change, reaction is spontaneous going to completion. Original state is not restored.                                                          |
| Thermal effect | Physical change can take place in the absence or presence of heat.<br>Above change absorbs heat in forward side and loses heat in backward side. | Chemical change initially endothermic (takes place with absorption of heat). Above change requires heat.                                                  |



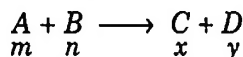
## Laws of Chemical Combination

### Law of Conservation of Mass

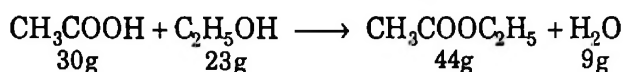
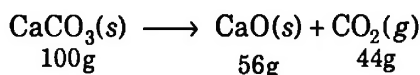
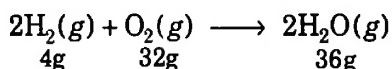
(Lavoisier-1789)

"As a result of chemical change, the total mass of the reactants is equal to the total mass of the products."

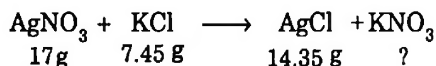
Thus, of masses  $m$  and  $n$  of reactants  $A$  and  $B$  react to form masses  $x$  and  $y$  of the products  $C$  and  $D$



Then,  $m + n = x + y$



### Numerical Problem Solving 1



What is mass of  $\text{KNO}_3$ ?

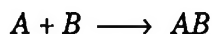
### Law of Definite or Constant Composition

(Proust-1799)

"A chemical substance always consists of the same elements combined together in the same proportions by mass."

If the elements  $A$  and  $B$  combine together to form the compound  $AB$ , then in whatever manner  $AB$  is formed, then it is always composed of these two elements and mass percentage of  $A$  and  $B$  remains constant.

$AB$  can be formed by two methods.



First method  $a\text{ g}$   $b\text{ g}$   $\frac{a}{b}$  thus, ratio of  $A$  and

$B$  in  $AB$  by mass

Second method  $x\text{ g}$   $y\text{ g}$   $\frac{x}{y}$

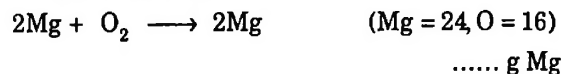
thus,  $\frac{a}{b} = \frac{x}{y}$

- $\text{H}_2\text{O}$  irrespective of its source has  $\text{H}$  and  $\text{O}$  in 1:8 mass ratio in pure state.

- $\text{CaCO}_3$  irrespective of its source has  $\text{Ca}$ ,  $\text{C}$  and  $\text{O}$  as 40%, 12%, 48% by mass.

### Numerical Problem Solving 2

12 g magnesium combines with 8 g oxygen to form magnesium oxide. If 32 g oxygen combines, what is the mass of magnesium combining with oxygen? Do they differ in composition.



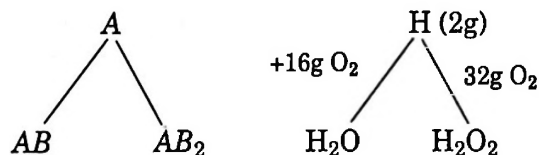
### Law of Multiple Proportions

(Dalton-1803)

"When one element combines with a second element to form two or more different compounds, the mass of one of the elements which combines with the constant mass of the other, bears a simple ratio to one another."

Simple ratio means whole number multiples

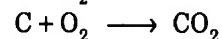
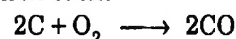
$A$  combines with  $B$  to form  $AB$  and  $AB_2$ . Then ratio of  $B$  (by mass in  $AB$  and  $AB_2$ ) that combines with a definite mass of  $A$  is in a simple multiple ratio.



- 2 g  $\text{H}_2$  combines with 16 g  $\text{O}_2$  to form 18 g  $\text{H}_2\text{O}$   
2g  $\text{H}_2$  combines with 32 g  $\text{O}_2$  to form 34 g  $\text{H}_2\text{O}_2$   
Thus, ratio of oxygen (by mass) that combines with 1 g  $\text{H}_2$  is 8 : 16 = 1 : 2

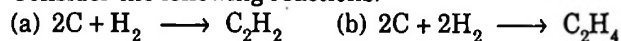
### Numerical Problem Solving 3

- Carbon and oxygen form two oxides carbon monoxide and carbon dioxide. What is the ratio of oxygen that combines with 1 g carbon in each?



Ratio = .....

- Consider the following reactions.



Is law of multiple proportions followed.

Yes/No

### Law of Reciprocal Proportions

(Richter-1792)

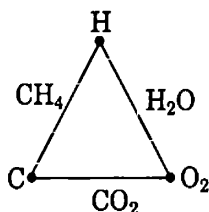
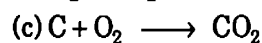
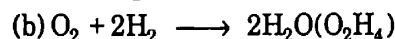
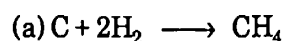
"The masses of two or more different elements which separately combine with a definite mass of another element are either the same as or are simple multiples of the masses of these different elements when they combine amongst themselves."

A combines with C to form AC

B combines with C to form BC

A combines with B to form AB

Then ratio of A and B by mass in AB is same as ratio of A and B, and AC and BC.



4 g  $H_2$  combines with 12 g carbon in (a)

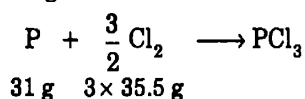
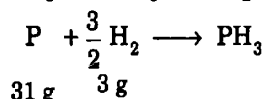
4 g  $H_2$  combines with 32 g oxygen in (b)

Thus, ratio of carbon and oxygen in (a) and (b) by mass that combines with a definite mass of  $H_2$  (in this case 4 g) =  $12:32 = 3:8$  in (c) 12 g carbon combines with 32 g oxygen thus ratio of carbon and oxygen (by mass) in  $CO_2$  is  $3:8$

| Compound | Elements | Mass ratio                                                                         |
|----------|----------|------------------------------------------------------------------------------------|
| $CH_4$   | C and H  | $\begin{array}{c} 3:1 \\ \curvearrowright 8:1 \\ \curvearrowright 3:8 \end{array}$ |
| $H_2O$   | O and H  |                                                                                    |
| $CO_2$   | C and O  |                                                                                    |

### Numerical Problem Solving 4

Phosphorus forms  $PH_3$  and  $PCl_3$  with  $H_2$  and  $Cl_2$  respectively.



In which ratio by mass  $H_2$  and  $Cl_2$  combine to form  $HCl$ ?

Ans. ....

### Law of Equivalent Proportions (Richter-1792)

“Elements combine in the ratio of their equivalent mass or in simple multiple of them.  
(Equivalent mass – Refer in this unit)”

Equivalent mass of hydrogen = 1

Equivalent mass of oxygen = 8

Equivalent mass of magnesium = 12

Equivalent mass of calcium = 20

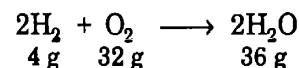
Equivalent mass of chlorine = 35.5



Ratio by mass    2g     $2 \times 35.5$  g     $2 \times 36.5$  g

$H_2$  and  $Cl_2$  combine in the mass ratio =  $2:2 \times 35.5$   
=  $1:35.5$

Thus, ratio is also the ratio of their equivalent masses.



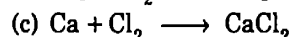
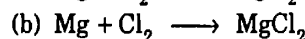
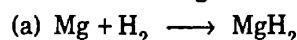
$H_2$  and  $O_2$  combine in the mass ratio =  $4:32 = 1:8$

This is also the ratio of their equivalent masses.

**Law of Reciprocal Proportion is a special case of Law of Equivalent Proportion**

### Numerical Problem Solving 5

Consider the following reactions ( $Mg = 24$ ,  $Cl = 35.5$ ,  $Ca = 40$ )



Equivalent mass of hydrogen is 1, derive equivalent mass of magnesium, chlorine and calcium.

Ans.  $Mg = \dots\dots$ ,  $Cl = \dots\dots$   $Ca = \dots\dots$

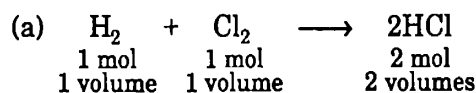
### Law of Gaseous Volume or Gay-Lussac's Law (Gay-Lussac-1808)

When gases combine together they do so in simple ratio by volume and the volume of the product formed (if gaseous), also bear a simple relation to the volume of the reacting gases, measured under the same conditions of temperature and pressure.

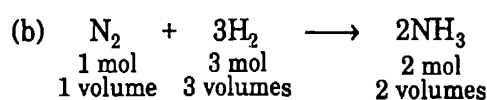
(1 mole of every gas at NTP = 22.4 L and equal moles occupy equal volumes)

#### Gaseous Reactions

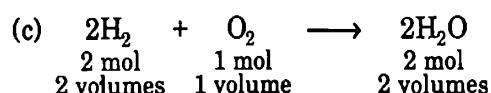
**R of V P  
Reactants**



1:1 : 2



1:3 : 2

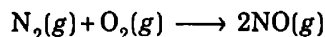


2:1 : 2

\*R of V = Ratio of volume, \*\*P = Product

### Numerical Problem Solving 6

Nitrogen combines with oxygen in the following reaction



What is ratio of the reactants and products?

- (a) By mass (b) By equivalent  
(c) By moles (d) By volume

| Ans. | N <sub>2</sub> | O <sub>2</sub> | NO    |
|------|----------------|----------------|-------|
| (a)  | .....          | .....          | ..... |
| (b)  | .....          | .....          | ..... |
| (c)  | .....          | .....          | ..... |
| (d)  | .....          | .....          | ..... |

## Dalton and Constitution of Matter

### Dalton Atomic Theory (1803)

- All elements are composed of minute particles called atoms, which do not undergo subdivision during chemical reactions and cannot be created or destroyed by any chemical process. (Taylor)
- Atoms of the same element are similar to one another in all respects and are equal in weights.
- Atoms of different elements have different masses (called atomic masses) and different properties.
- Chemical combination between two or more elements takes place by interaction of their atoms in simple numerical proportions (as 1 : 1; 1 : 2; 1 : 3; etc.)

|                                                         | Ratio |
|---------------------------------------------------------|-------|
| $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$  | 1 : 1 |
| $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$ | 1 : 3 |
| $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$     | 1 : 1 |

- Combining masses of the elements represent the combining masses of the atoms.  
Dalton atomic, theory can explain various laws of chemical combination.

### Limitations and Defects of Dalton's Atomic Theory

- It can explain the laws of chemical combination by weight, but it fails to explain Gay-Lussac's law of gaseous volume.
- Distinction between the ultimate particles of an element and the smallest particle of a compound, both of which are made of atoms, could not be made.
- It assumes that atoms of same element are like and have same mass. But this is not true for isotopes (two

or more atoms with same atomic number but different atomic mass are called isotopes).

- $^{12}_6\text{C}$ ,  $^{13}_6\text{C}$ ,  $^{14}_6\text{C}$ , have atoms of different masses.  $^1_1\text{H}$ ,  $^2_1\text{H}$ ,  $^3_1\text{H}$  have atoms of different masses.

### Avogadro's Hypothesis

Berzelius assumed "equal volumes of different gases under identical conditions of temperature and pressure contain the same number of atoms (The word atom was at that time used for both elements and compounds as molecule was not thought of). We consider the formation of  $\text{H}_2\text{O}(\text{g})$  from  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$

|                  |                         |                         |                   |                                 |
|------------------|-------------------------|-------------------------|-------------------|---------------------------------|
|                  | $2\text{H}_2(\text{g})$ | $+\text{O}_2(\text{g})$ | $\longrightarrow$ | $2\text{H}_2\text{O}(\text{g})$ |
|                  | 2 volume                | 1 volume                |                   | 2 volume                        |
| <b>Berzelius</b> | 2 atoms                 | 1 atom                  |                   | 2 atoms                         |
|                  | 1 atom                  | $\frac{1}{2}$ atom      |                   | 1 atom                          |

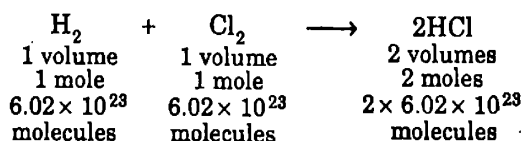
1 atom of  $\text{H}_2$  combines with  $1/2$  atom of  $\text{O}_2$ . This allows atom to be divisible. This is against Dalton's atomic theory. Hence, Berzelius hypothesis was discarded. Failure led to assume that gases exist in polyatomic state (diatomic, triatomic etc.) and ultimate particles which can exist in the free state were defined as **molecule**. Avogadro's hypothesis is based on molecules :

"Equal volume of all gases under the same conditions of temperature and pressure contain the same number of molecule".

Avogadro's hypothesis led to

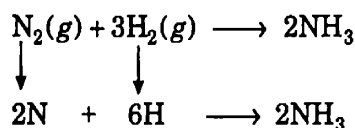
- the word molecule and made the distinction between atoms and molecules.
- conclude that molecules of hydrogen, chlorine, oxygen, nitrogen and fluorine are diatomic.
- conclude that molecular weight =  $2 \times$  vapour density.
- Conclude that one gram-molecular mass (molecular weight) has volume 22.4 L ( $22.4 \times 10^{-3} \text{ m}^3$ ) at NTP (pressure = 1 atm and  $T = 273.15 \text{ K}$ )

Number of molecules present in amount equal to molecular weight (which we shall call one mole) are  $6.02 \times 10^{23}$  (called Avogadro's number)



## Dalton's Theory as Modified by Avogadro's Hypothesis

1. Substances (elements and compounds) consist of molecules which are composed of indivisible particles called atoms. Molecules are capable of independent existence and are divisible into atoms.
2. Molecules of a particular substance are similar to one another; with identical properties and mass. Molecules of one substance are different from those of other substances.
3. When there is chemical reaction between two or more substances, the molecules of each substance are first disintegrated into atoms which combine together to produce new molecules of the new substances.



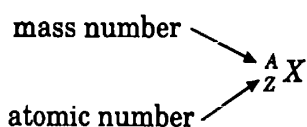
## Atomic Number, Mass Number and Isotopes

- All atoms can be identified by the number of protons and neutrons they contain. *The atomic number (Z) is the number of protons in the nucleus of each atom of an element.*
- In a neutral atom the number of protons is equal to the number of electrons present in the atom.
- The chemical identity of an atom can be determined solely from its atomic number. For example atomic number of oxygen is 8. This means each neutral oxygen atom has 8 protons and 8 electrons.
- The *mass number (A) is the total number of neutrons and protons present in the nucleus of an atom of an element.*
- Except for hydrogen (which has only one proton), all atomic nuclei contain both protons and neutrons.
- The mass number is given by

$$\text{mass number (A)} = P + N = Z + N$$

$$= \text{atomic number} + \text{no. of neutrons}$$

$$\text{Thus, } N (\text{number of neutrons}) = A - Z$$



- Atomic number, number of neutrons, and mass number all must be positive integers (whole numbers).
- Atoms of a given element do not all have the same mass. Most elements have two or more **isotopes** (atoms that have the same atomic number but

different mass numbers). There are three isotopes of hydrogen

|                  |           |     |     |
|------------------|-----------|-----|-----|
| ${}^1_1\text{H}$ | hydrogen  | 1 P | 0 N |
| ${}^2_1\text{H}$ | deuterium | 1 P | 1 N |
| ${}^3_1\text{H}$ | tritium   | 1 P | 2 N |

Thus, isotopes have different number of neutrons.

- The chemical properties of an element are determined primarily by the protons and electrons in its atoms; neutrons do not take part in chemical changes under normal conditions. Therefore, isotopes of the same element have similar chemical reactions.

## Atomic Weight

**The atomic weight of an element is the smallest weight of it present in the molecular weights of its compounds.**

It may also be defined thus —

The atomic weight of an element is a number which expresses how many times the weight of one atom of the element is greater than the weight of one atom of hydrogen.

At. wt. of an element

$$= \frac{\text{wt. of 1 atom of the element}}{\text{wt. of 1 atom of hydrogen}}$$

Thus, the atomic weights are not the actual weights of atoms but the relative weights of the atoms of various elements expressed in terms of hydrogen as unit. Hence, when we say that the atomic weight of nitrogen is 14, we mean that an atom of nitrogen is 14 times heavier than an atom of hydrogen; that is to say, if the weight of one atom of hydrogen is taken as unit, the weight of 1 atom of nitrogen will be 14 times the weight of 1 atom of hydrogen.

Now a days the standard for atomic weight is  $\text{C}^{12}$ . On this basis the atomic weight may be defined as :

**The atomic weight of an element is a number which indicates as to how many times an element of that element is heavier as compared with 1/12 of the mass of an atom of  $\text{C-12}$  ( ${}^{12}_6\text{C}$ ).**

$$\text{At. wt. of an element} = \frac{\text{wt. of an atom}}{\frac{1}{12} \times \text{wt. of an atom of } {}^{12}\text{C}}$$

The gram atomic weight (or the gram-atom) of an element is its atomic weight expressed in grams. Thus, 1 g-atom of magnesium stands for 24 g of Mg.

The French chemists Dulong and Petit in 1819 found out that the product of the specific heat of an element in the solid state and its atomic weight is constant, and is equal to 6.4.

$$\text{Specific heat} \times \text{atomic weight} = 6.4 (\text{approx.})$$

## Atomic Mass Unit

An early observation regarding atomic weight was that carbon and hydrogen have relative atomic masses, also traditionally called **atomic weight**, AW, of approximately 12 and 1, respectively. Thousands of experiments on the composition of compounds have resulted in the establishment of scale of relative weights based on the atomic mass unit (amu), which is defined as.

**“Exactly 1/12 of the mass of an atom of a particular kind of carbon atom, called carbon-12. Its value is  $1.66054 \times 10^{-24}$  g.**

On this scale, the atomic weight of hydrogen is 1.00794 amu

Sodium is 22.989768 amu – 23 times of H

Magnesium is 24.3050 amu – 24 times of H

- amu is also called dalton (Da).
- Mass of one  $^{12}_6\text{C}$  atom = 12 amu (exactly)

$$1 \text{ amu} = \frac{\text{mass of one } ^{12}_6\text{C atom}}{12}$$

$$= 1.66054 \times 10^{-24} \text{ g}$$

- Thus, mass of one H-atom =  $\frac{1}{N_0} = 1 \text{ amu}$

$$\text{mass of one O-atom} = \frac{16}{N_0} = 16 \text{ amu}$$

## Average Atomic Weight

Average mass number of natural occurring element containing two or more isotopes is given by

$$\bar{A} = \frac{\sum AX}{\sum X} = \frac{A_1X_1 + A_2X_2 + \dots}{X_1 + X_2 + \dots}$$

where,  $A_1, A_2, \dots$  are mass numbers of the different isotopes with percentage or ratios as  $X_1, X_2, \dots$

If  $^{35}_{17}\text{Cl}$  and  $^{37}_{17}\text{Cl}$  are two isotopes of chlorine in the ratio of 3 : 1, then average mass number of Cl is

$$\bar{A}(\text{Cl}) = \frac{35 \times 3 + 37 \times 1}{3 + 1} = 35.5$$

**Illustration 1** A divalent cation (Atomic number  $Z$ ) is isoelectronic of  $\text{CO}_2$  and has  $(Z + 2)$  neutrons. What is ionic mass of divalent cation?

**Solution** A divalent cation ( $M^{2+}$ ) has as many as electrons as  $\text{CO}_2 = 6 + 16 = 22$

Hence, ( $Z$ ) atomic number of

$$M^{2+} = 22 + 2 = 24$$

or number of protons ( $P$ ) in  $M^{2+} = 24$

number of neutrons ( $N$ ) in  $M^{2+} = Z + 2 = 24 + 2 = 26$

$\therefore$  ionic mass of  $M^{2+} = P + N = 24 + 26 = 50$

**Illustration 2** Ionic mass of  $X^{2-}$  is 16. It has 8 neutrons. Determine the number of its (a) protons (b) number of electrons and (c) atomic number  $Z$ .

**Solution** Ionic mass of  $X^{2-} = 16$ , neutrons = 8

(a) protons =  $16 - 8 = 8$

$\therefore$  electrons in neutral  $X = 8$

(b)  $X$  gains two electrons to form  $X^{2-}$ ,

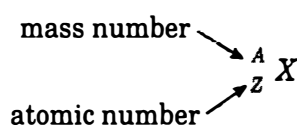
hence, number of electrons is  $X^{2-} = 8 + 2 = 10$

(c)  $Z = \text{atomic number} = 8$

**Illustration 3** Write the appropriate symbol for each of the following isotopes.

(a)  $Z = 74, A = 186$  (b)  $Z = 80, A = 201$

**Solution** For any isotope, system is



(a)  $Z = 74, A = 186$   $^{186}_{74}\text{X}$

(b)  $Z = 80, A = 201$   $^{201}_{80}\text{X}$

**Illustration 4**  $^{10}_5\text{B}$  and  $^{11}_5\text{B}$  are two isotopes of boron. If average mass number is 10.2, what is the percentage of each?

**Solution** Let the percentage of  $^{10}_5\text{B} = x$

then percentage of  $^{11}_5\text{B} = (100 - x)$

$$\text{Average mass number } \bar{A} = \frac{A_1X_1 + A_2X_2}{X_1 + X_2}$$

$$\therefore 10.2 = \frac{10x + 11(100 - x)}{x + 100 - x}$$

$$10.2 = \frac{10x + 1100 - 11x}{100}$$

$$x = 80$$

Thus, percentage of  $^{10}_5\text{B} = 80\%$

and percentage of  $^{11}_5\text{B} = 20\%$

## Target Practice 1

Avogadro's number =  $6.02 \times 10^{23}$  atoms/mol

1 mole of a gas at STP occupies 22.4 L

- How many atoms of oxygen are there in 18 g of water? .....
- How many atoms of hydrogen are there in 18 g of water?
- How many molecules of  $H_2O$  are there in 18 g of water? .....
- What is the mass of 1 mole of  $O_2$ ? .....
- What is the mass of 1 molecule of  $O_2$ ? .....
- What is the mass of 2 moles of  $H_2SO_4$ ? .....
- What is the density (mass/volume) of  $O_2$  at STP? .....

- 3 L of a gas weighs 2 g. What is the molecular mass? .....
- What volume does 22 g of  $CO_2$  at STP occupy? .....
- How many atoms of hydrogen are in 67.2 L of  $H_2$  at STP? .....
- You are given 1.0 g samples of He, Fe and C. Which contains the largest number of atoms? Which contains the smallest? (He = 4, Fe = 56, C = 12)

**Note:** Avogadro's number =  $6.02 \times 10^{23}$  atoms/mol

1 mole of a gas at STP occupies 22.4 L

## Answers

- $6.02 \times 10^{23}$
- $1.204 \times 10^{24}$
- $6.02 \times 10^{23}$
- 32 g
- $5.32 \times 10^{-23}$  g
- 196 g
- 1.43 g/L
- 14.9 g/L
- 11.2 L
- $3.612 \times 10^{24}$

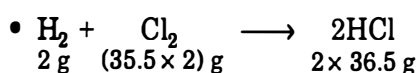
- He =  $\frac{N_0}{4}$ , Fe =  $\frac{N_0}{56}$ , C =  $\frac{N_0}{12}$   
He (Largest)      Fe (smallest)

## Equivalent Weight

It is also called the chemical equivalent (or simply equivalent) or the combining weight.

The weight of an element which can combine with or displace from a compound **1 part by weight of hydrogen**, or **8 parts by weight of oxygen** or **35.5 parts by weight of chlorine** is called the equivalent weight of the element.

**1 part by weight of hydrogen is actually the reference weight.**

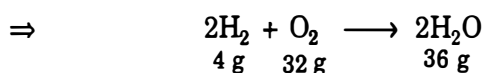


$\Rightarrow$  2 g hydrogen is equivalent ( $\equiv$ ) to 71 g chlorine ( $Cl_2$ )

thus, 1 g hydrogen is equivalent to ( $\equiv$ ) 35.5 g  $Cl_2$

Thus, equivalent weight of  $Cl_2$  = 35.5 g equivalent<sup>-1</sup>

and also equivalent weight of HCl = 36.5 g equivalent<sup>-1</sup>



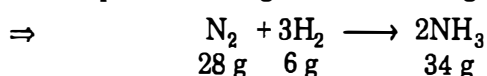
4 g hydrogen  $\equiv$  32 g oxygen

Thus, 1 g hydrogen  $\equiv$  8 g oxygen

Thus, equivalent weight of oxygen

= 8 g equivalent<sup>-1</sup>

Thus equivalent weight of water = 9 g equivalent<sup>-1</sup>



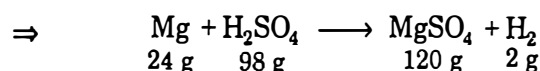
6 g hydrogen  $\equiv$  28 g nitrogen and 34 g ammonia

Thus, 1 g hydrogen

$\equiv \frac{28}{6}$  (= 4.66 g) nitrogen and  $\frac{34}{6}$  (5.66 g) ammonia.

Thus, equivalent weight of nitrogen = 4.66 g equivalent<sup>-1</sup>

and equivalent weight of ammonia = 5.66 g equivalent<sup>-1</sup>



2 g  $H_2$  is displaced by 24 g Mg

Thus, 1 g  $H_2$  is displaced by 12 g Mg

Thus, equivalent weight of magnesium

= 12 g equivalent<sup>-1</sup>

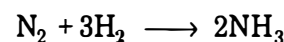
Also, 2 g  $H_2$  is displaced by 98 g  $H_2SO_4$

Thus, 1 g  $H_2$  is displaced by 49 g  $H_2SO_4$

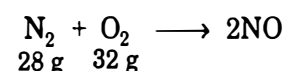
Thus, equivalent weight of  $H_2SO_4$  = 49 g equivalent.

## DEEP Focus

Equivalent weight is not a fixed quantity. It varies reaction to reaction.



Equivalent weight of nitrogen ( $N_2$ ) as equivalent to 1 g  $H_2$  = 4.66 g equivalent<sup>-1</sup>



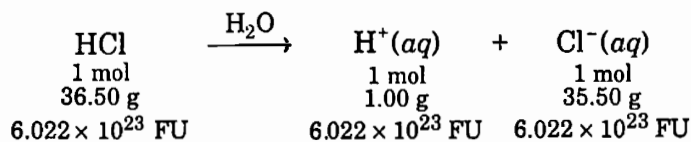
32 g oxygen  $\equiv$  28 g nitrogen

Thus, 8 g oxygen  $\equiv$  7 g nitrogen

Thus, equivalent weight of nitrogen

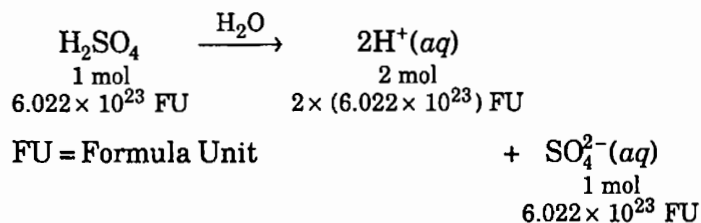
= 7 g equivalent<sup>-1</sup>

In acid-base reactions, one **equivalent weight**, or **equivalent (eq)**, of an acid is defined as the mass of acid (in grams) that will furnish  $6.022 \times 10^{23}$  hydrogen ions (1 mole) or that will react with  $6.022 \times 10^{23}$  hydroxide ions (1 mole). One mole of an acid contains  $6.022 \times 10^{23}$  formula units of the acid.



We observe that one mole of HCl can produce  $6.022 \times 10^{23}$   $\text{H}^+$ , hence one mole of HCl is one equivalent. The same is true for all monoprotic acids (with one ionisable  $\text{H}^+$ )

Sulphuric acid ( $\text{H}_2\text{SO}_4$ ) is a diprotic acid. One molecule of  $\text{H}_2\text{SO}_4$  can furnish  $2\text{H}^+$  ions



Thus, equation shows that one mole  $\text{H}_2\text{SO}_4$  can produce  $2(6.022 \times 10^{23})$   $\text{H}^+$  ions therefore, one mole of  $\text{H}_2\text{SO}_4$  is two equivalent weights in all reactions in which both acidic hydrogen ions react.

One **equivalent weight** of a base is defined as the mass of the base (expressed in grams) that will furnish  $6.022 \times 10^{23}$  hydroxide ions or the mass of the base that will react with  $6.022 \times 10^{23}$  hydrogen ions.

Detailed study of Equivalent weights based on redox reaction are taken in unit-3

### Numerical Problem Solving 7

- (i) Taking equivalent weight of hydrogen as (1) and that of oxygen as (8) derive equivalent weights of the underlined.
  - (a)  $\text{Mg} + \text{H}_2 \longrightarrow \underline{\text{MgH}_2}$  .....
  - (b)  $\text{Mg} + \frac{1}{2} \text{O}_2 \longrightarrow \underline{\text{MgO}}$  .....
  - (c)  $\text{C} + \text{O}_2 \longrightarrow \underline{\text{CO}_2}$  .....
  - (d)  $\frac{1}{2} \text{N}_2 + \text{O}_2 \longrightarrow \underline{\text{NO}_2}$  .....
- (ii) How many equivalents are in (based on ionization)?
  - (a) 3.65 g HCl ( $\rightleftharpoons \text{H}^+ + \text{Cl}^-$ ) .....
  - (b) 9.8 g  $\text{H}_2\text{SO}_4$  ( $\rightleftharpoons 2\text{H}^+ + \text{SO}_4^{2-}$ ) .....
  - (c) 9.8 g of  $\text{H}_3\text{PO}_4$  ( $\rightleftharpoons 3\text{H}^+ + \text{PO}_4^{3-}$ ) .....
- (iii) Cobalt has three radioactive isotopes used in medical studies. Atoms of these isotopes have 30, 31 and 33 neutrons, respectively. Give the symbol for each of these isotopes .....

## The Mole

You are already familiar with the dozen (12 items) and the gross (144 items).

The SI unit for amount is the **mole**, abbreviated **mol**. It is defined as the amount of substance that contains as many entities (atoms, molecules, or other particles) as there are atoms in exactly 0.012 kg of pure carbon-12 atoms. Many experiments have refined the number, and the currently accepted value is

$$1 \text{ mole} = 6.0221367 \times 10^{23} \text{ particles}$$

One mole is always associated with a chemical formula and refers to Avogadro's number of particles. It is designated by  $N_0$

$$N_0 = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$\begin{aligned}
 16 \text{ g oxygen atom} &= 1 \text{ mole of oxygen atom} \\
 &= 6.022 \times 10^{23} \text{ atoms}
 \end{aligned}$$

$$\begin{aligned}
 32 \text{ g oxygen gas} &= 1 \text{ mole of oxygen (O}_2\text{) gas} \\
 &= 6.022 \times 10^{23} \text{ oxygen molecules} \\
 &= 2 \times 6.022 \times 10^{23} \text{ oxygen atoms}
 \end{aligned}$$

### DEEP Focus

When to use 1.008 g/mol for the molar mass of hydrogen and when to use 2.016 g/mol?

The statement, "a mole of hydrogen" is ambiguous; you should always say either a mole of hydrogen *atoms* or a mole of hydrogen *molecules*. Better still write **1 mol H** or **1 mol H<sub>2</sub>**. If you do this is, then you will see that the molar masses should be expressed as **1.008 g H/mol H** and **2.016 g H<sub>2</sub>/mol H<sub>2</sub>**. This distinction is very much like the distinction between one dozen socks and one dozen pairs of socks (that is, the H atom is analogous to a single sock and the H<sub>2</sub> molecule to a pair of socks).

**The mass of one mole of atoms of pure element in grams is numerically equal to atomic weight of that element in amu.** This is also called **molar mass** of the element; its **units are grams/mole**

Molar mass of a substance is the mass in gram of one mole of that substance.

$$\text{Moles of substance} = \frac{\text{mass in grams}}{\text{molar mass in grams/mole}}$$

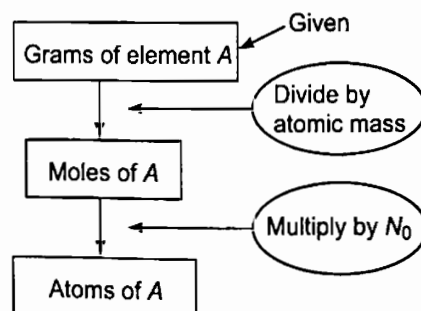


Fig. 1.3

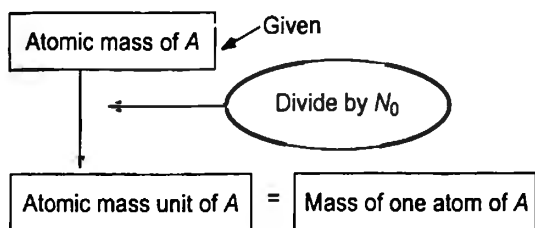


Fig. 1.4

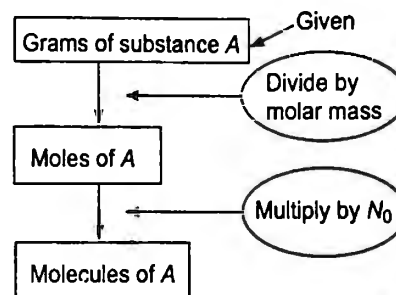


Fig. 1.5

Table 1.2 One Mole of Some Ionic Compounds

| Compound           | Formula weight | A sample with a mass of 1 mole                          | Contains                                                                                                                                                                                             |
|--------------------|----------------|---------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Sodium chloride    | 58.44          | 58.44 g NaCl                                            | $6.022 \times 10^{23}$ Na <sup>+</sup> ions or 1 mole of Na <sup>+</sup> ions<br>$6.022 \times 10^{23}$ Cl <sup>-</sup> ions or 1 mole of Cl <sup>-</sup> ions                                       |
| Calcium chloride   | 111.0          | 111.0 g CaCl <sub>2</sub>                               | $6.022 \times 10^{23}$ Ca <sup>2+</sup> ions or 1 mole of Ca <sup>2+</sup> ions<br>$2(6.022 \times 10^{23})$ Cl <sup>-</sup> ions or 2 moles of Cl <sup>-</sup> ions                                 |
| Aluminium sulphate | 342.1          | 342.1 g Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | $2(6.022 \times 10^{23})$ Al <sup>3+</sup> ions or 2 moles of Al <sup>3+</sup> ions<br>$3(6.022 \times 10^{23})$ SO <sub>4</sub> <sup>2-</sup> ions or 3 moles of SO <sub>4</sub> <sup>2-</sup> ions |

**Illustration 4** Sulphur is a non-metallic element. Its presence in coal gives rise to the acid-rain phenomenon. How many sulphur atoms are in 10 kg of coal sample containing 1% sulphur. (S = 32 g mol<sup>-1</sup>)

**Solution** 10 kg coal =  $10 \times 10^3$  g coal  

$$= \frac{10 \times 10^3 \times 1}{100} \text{ g sulphur}$$

$$= 10^2/32 \text{ mol sulphur}$$

$$= (10^2/32) \times 6.022 \times 10^{23} \text{ atoms of sulphur}$$

$$= 1.882 \times 10^{24} \text{ sulphur atoms}$$

**Illustration 5** How many H atoms are present in 25.6 g of urea [(NH<sub>2</sub>)<sub>2</sub>CO], having molar mass of 60 g mol<sup>-1</sup>?

**Solution** 25.6 g urea =  $\frac{25.6}{60}$  mol urea  

$$= \frac{25.6}{60} \times 6.022 \times 10^{23} \text{ molecules}$$

$$= \frac{25.6}{60} \times 6.022 \times 10^{23} \times 4 \text{ H atoms}$$

$$= 1.0274 \times 10^{24} \text{ H atoms}$$

**Illustration 6** Mass of one atom of an element X is  $2.32481 \times 10^{-23}$  g. Express this in amu.

**Solution** Let atomic mass of the element be = A

Number of atoms in one mol of X =  $N_0$

Hence, mass of one atom of X =  $\frac{A}{N_0}$

$$\therefore \frac{A}{N_0} = 2.32481 \times 10^{-23} \text{ g}$$

$$\therefore A = 2.32481 \times 10^{-23} \times N_0$$

$$= 2.32481 \times 10^{-23} \times 6.022 \times 10^{23}$$

$$= 14$$

Hence, mass of one atom of X =  $\frac{14}{N_0} = 14 \text{ amu}$

## Target Practice 2

1. Which of the following has the greatest mass?

- 200 molecules of water
- 100 atoms of Fe
- 200 molecules of O<sub>2</sub>
- 200 molecules of CH<sub>4</sub>

2. If the fertilizers listed below are priced according to their nitrogen content, which will be the least expensive per 50 kg bag?

- Urea (NH<sub>2</sub>)<sub>2</sub>CO
- Ammonia NH<sub>3</sub>

(c) Ammonium nitrate NH<sub>4</sub>NO<sub>3</sub>

(d) Guanidine HNC(NH<sub>2</sub>)<sub>2</sub>

3. One atom of an element has a mass of  $9.123 \times 10^{-23}$  g.

There is only one isotope of the element. The element is

- chlorine
- chromium
- magnesium
- manganese

4. One mole of (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> contains

- one mole of nitrogen
- four moles of hydrogen
- one mole of chromium
- seven moles of oxygen



## 12 Essential Inorganic Chemistry

- Which of the following statements are true?
  - 1 mole H atoms =  $6.02 \times 10^{23}$  H atoms
  - $6.02 \times 10^{23}$  H atoms have a mass of 1.008 g
  - The formula mass of  $O_2$  = 32.00 amu
  - All of the above are true
- Which of the following has the largest mass of carbon per gram?
  - $H_2CO_3$
  - $C^{+}CO_2H$
  - $CH_3OH$
  - $CH_3CH_2OH$
- 1 g urea ( $NH_2CONH_2$ ), 1 g acetic acid ( $CH_3COOH$ ) and 1 g formaldehyde ( $HCHO$ ) will have H-atoms in the ratio
  - 2 : 2 : 1
  - 1 : 1 : 2
  - 1 : 1 : 1
  - 1 : 2 : 1
- There are  $\frac{N_0}{2}$  atoms in given quantity of carbon-12. Same number of atoms are present in
  - 6 g Mg
  - 12 g Mg
  - 16 g  $O_2$
  - 8 g  $CH_4$
- Mass of  $O_2$ ,  $N_2$  and  $CH_4$  containing equal moles will be in the ratio of
  - 16 : 14 : 16
  - 8 : 7 : 4
  - 1 : 1 : 1
  - 4 : 7 : 4
- Which has maximum volume at STP? (1 mole of a gas = 22.4 L at STP)
  - 1.6 g  $CH_4$
  - $6.02 \times 10^{22}$   $N_2$  molecules
  - 4.4 g  $CO_2$
  - Equal

### Answers

- 200 molecules  $H_2O = \frac{200}{N_0} \text{ mol } H_2O = \frac{3600}{N_0} \text{ g } H_2O$
  - 100 atoms  $Fe = \frac{100}{N_0} \text{ mol } Fe = \frac{100}{N_0} \times 56 = \frac{5600}{N_0} \text{ g } Fe$
  - 200 molecules  $O_2 = \frac{200}{N_0} \text{ mol } O_2 = \frac{6400}{N_0} \text{ g } O_2$
  - 200 molecules  $CH_4 = \frac{200}{N_0} \times 10 \text{ g } CH_4 = \frac{3200}{N_0} \text{ g } CH_4$
 Thus, (c)
- (c)
- $9.123 \times 10^{-23} \times 6.02 \times 10^{23} \text{ g mol}^{-1} \approx 55$   
Mn. Thus, (d)
- (d)    5. (d)
- $H_2CO_3$ ,  $\frac{12}{62} \text{ g carbon}$
  - $CH_3CO_2H$ ,  $\frac{24}{60} \text{ g carbon}$
  - $CH_3OH$ ,  $\frac{12}{32} \text{ g carbon}$
  - $CH_3CH_2OH$ ,  $\frac{24}{40} \text{ g carbon (max.)}$
 Thus, (d)
- $1 \text{ g urea} = \frac{1}{60} \text{ mol} = \frac{4N_0}{60} \text{ H-atom}$   
 $1 \text{ g acetic acid} = \frac{1}{60} \text{ mol} = \frac{4N_0}{60} \text{ H-atom}$   
 $1 \text{ g formaldehyde} = \frac{1}{30} \text{ mol} = \frac{2N_0}{30} \text{ H-atom} = \frac{4N_0}{60} \text{ H-atom}$   
 Thus, 1 : 1 : 1  
 Thus, (c)
- (b)    9. (b)    10. (d)

## Practice Exercise 1

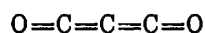
- Substances X and Y are colourless gases obtained by combination of sulphur and oxygen. Substance X results from combination of 6.00 g of sulphur with 6.00 g of oxygen and substance Y results from combination of 8.60 g of sulphur with 12.9 g of oxygen. Show that the mass ratios in the two substances are simple multiples of each other.
- In addition to carbon monoxide ( $CO$ ) and carbon dioxide ( $CO_2$ ), there is a third compound of carbon called carbon suboxide. If a 2.500 g sample of carbon suboxide contains 1.32 g of C and 1.18 g of O, show that the law of multiple proportions is followed. What is possible formula of carbon suboxide?
- In which one of the following pairs do the two species resemble each other most closely in chemical properties? Explain.
  - $^1_1H$  and  $^1_1H^+$
  - $^{14}_7N$  and  $^{14}_7N^{3-}$
  - $^{12}_6C$  and  $^{13}_6C$
- One isotope of a metallic element has mass number 65 and 35 neutrons in the nucleus. The cation derived from the isotope has 28 electrons. Write the symbol for this cation.
- Which of the following symbols provides more information about the atom:  $^{23}Na$  or  $^{23}_{11}Na$ ? Explain.
- Fill in the blanks in the following table :
 

| Symbol     | $^{54}_{26}Fe$ |   |    |     |     |
|------------|----------------|---|----|-----|-----|
| Protons    | 5              | — | —  | 79  | 86  |
| Neutrons   | 6              | — | 16 | 117 | 136 |
| Electrons  | 5              | — | 18 | 79  |     |
| Net charge | —              | — | -3 |     | 0   |
- How many H atoms are in 6.0 g of isopropanol  $C_3H_8O$ ?
- How many moles of cobalt atoms are there in  $6.022 \times 10^9$  Co atoms?
- The density of water is 1.00 g/mL at 4°C. How many water molecules are present in 2.56 mL water at this temperature?
- Aspirin has the formula  $C_9H_8O_4$ . How many moles of aspirin are there in a tablet weighing 500 mg? How many molecules?
- What is molecular weight of chloroform if 0.0275 mol weighs 3.28 g?
- An average cup of coffee contains about 125 mg caffeine,  $C_8H_{10}N_4O_2$ . How many moles of caffeine are in a cup? How many molecules?
- Select correct alternate. Only **one** alternate is correct.
  - In which case purity of the substance is 100%?
    - 1 mole of  $CaCO_3$  gave 11.2 L  $CO_2$  (at STP)

- (b) 1 mole of  $\text{MgCO}_3$  gave 40.0 g  $\text{MgO}$   
 (c) 1 mole of  $\text{NaHCO}_3$  gave 4 g  $\text{H}_2\text{O}$   
 (d) 1 mole of  $\text{Ca}(\text{HCO}_3)_2$  gave 1 mole  $\text{CO}_2$
- (B) Consider following laws of chemical combination with examples:  
 I : Law of multiple proportion :  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$   
 II : Law of reciprocal proportion :  $\text{H}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$   
 Which is correct with examples?  
 (a) I and II (b) I only  
 (c) II only (d) None of these
- (C)  $\text{H}_2\text{S}$  contains 94.11% sulphur;  $\text{SO}_2$  contains 50% oxygen and  $\text{H}_2\text{O}$  contains 11.11% hydrogen. Thus,  
 (a) law of multiple proportion is followed  
 (b) law of reciprocal proportion is followed  
 (c) law of conservation of mass is followed  
 (d) all of the above are followed
- (D) Sodium combines with  $^{35}_{17}\text{Cl}$  and  $^{37}_{17}\text{Cl}$  to give two samples of sodium chloride. Their formation follows the law of  
 (a) gaseous diffusion (b) conservation of mass  
 (c) reciprocal proportion (d) none of these
- (E) According to Dalton's atomic theory, the smallest particle in which matter can exist is called  
 (a) an atom (b) an ion  
 (c) an electron (d) a molecule
- (F)  $M^{2+}$  ion is isoelectronic of  $\text{SO}_2$  and has  $(Z + 2)$  neutrons ( $Z$  is atomic number of  $M$ ). Thus, ionic mass of  $M^{2+}$  is  
 (a) 70 (b) 66  
 (c) 68 (d) 64
- (G)  $X^+$ ,  $Y^{2+}$  and  $Z^-$  are isoelectronic of  $\text{CO}_2$ . Increasing order of protons in  $X^+$ ,  $Y^{2+}$  and  $Z^-$  is  
 (a)  $X^+ = Y^{2+} = Z^-$  (b)  $X^+ < Y^{2+} < Z^-$   
 (c)  $Z^- < X^+ < Y^{2+}$  (d)  $Y^{2+} < X^+ < Z^-$
- (H)  $X^-$ ,  $Y^{2-}$  and  $Z^{3-}$  are isotonic and isoelectronic. Thus, increasing order of atomic number of  $X$ ,  $Y$  and  $Z$  is  
 (a)  $X < Y < Z$  (b)  $Z < Y < X$   
 (c)  $X = Y = Z$  (d)  $Z < X < Y$
- (I) If each O-atom has two equivalents, volume of one equivalent of  $\text{O}_2$  gas at STP is  
 (a) 22.4 L (b) 11.2 L  
 (c) 5.6 L (d) 44.8 L
- (J) Each drop of  $\text{H}_2\text{O}$  has 0.018 mL at room temperature. Number of  $\text{H}_2\text{O}$  molecules in one drop is  
 (a)  $1 \times 10^{-3}$  (b)  $6.02 \times 10^{20}$   
 (c)  $22.4 \times 10^{-3}$  (d)  $6.02 \times 3 \times 10^{23}$
- (K) 1 g  $\text{CH}_4$  and 4 g of compound  $X$  have equal number of moles. Thus, molar mass of  $X$  is  
 (a)  $16 \text{ g mol}^{-1}$  (b)  $32 \text{ g mol}^{-1}$   
 (c)  $4 \text{ g mol}^{-1}$  (d)  $64 \text{ g mol}^{-1}$

## Answers

1.  $X : \text{SO}_2$                       Ratio  
        $Y : \text{SO}_3$                       S O  
                                          1 : 2  
                                          1 : 3  
 Thus, O atom in  $\text{SO}_2$  and  $\text{SO}_3$  are simple multiple of each other.
2. Carbon suboxide  $\text{C}_3\text{O}_2$



3. (c)    4.  $^{65}_{30}\text{M}^{2+}$     5.  $^{23}_{11}\text{Na}$

| 6. Symbol  | $^{11}_5\text{B}$ | $^{54}_{26}\text{Fe}$ | $^{31}_{15}\text{P}^{3-}$ | $^{196}_{79}\text{Au}$ | $^{222}_{86}\text{Rn}$ |
|------------|-------------------|-----------------------|---------------------------|------------------------|------------------------|
| Protons    | 5                 | 26                    | 15                        | 79                     | 86                     |
| Neutrons   | 6                 | 28                    | 16                        | 117                    | 136                    |
| Electrons  | 5                 | 26                    | 18                        | 79                     | 86                     |
| Net charge | zero              | zero                  | -3                        | zero                   | zero                   |

7.  $4.8176 \times 10^{23}$  H atoms  
 8.  $10^{-14}$  mol cobalt atoms  
 9.  $8.56 \times 10^{22}$  water molecules  
 10.  $2.78 \times 10^{-3}$  mol,  $1.67 \times 10^{21}$  molecules  
 11.  $119.27 \text{ g mol}^{-1}$   
 12.  $6.44 \times 10^{-4}$  mol,  $3.88 \times 10^{20}$   $N_0$  molecules  
 13. A. (b)    B. (a)  
       C. (b)    D. (d)  
       E. (a)    F. (a)  
       G. (c)    H. (b)  
       I. (c)    J. (b)  
       K. (d)

## Per cent Composition and Empirical Formula

- The per cent composition of a compound is expressed by identifying the elements present and giving the mass per cent of each.
- By knowing per cent composition of compound makes it possible to calculate the chemical formula of the compounds. The method involved is to find the relative number of mole of each element in the compound and then use & numbers to establish the mole ratios of the elements.
- A formula derived up to above stage from data about per cent composition, is called an **empirical formula**

because it tells the ratios of atoms in a compound. The **simplest** or **empirical formula** for a compound is the smallest whole number ratio of atoms present.

For **molecular compounds** the **molecular formula** indicates the actual number of atoms present in a molecule of the compound. It may be the same as the simplest formula or else whole-number multiple of it. Simplest and molecular formulae of water are both  $\text{H}_2\text{O}$ . However for hydrogen peroxide they are  $\text{HO}$  and  $\text{H}_2\text{O}_2$  respectively.

$$\text{Multiple } n = \frac{\text{molecular weight}}{\text{empirical formula weight}}$$

## 14 Essential Inorganic Chemistry

- Molecular formula = (empirical formula)<sub>n</sub>

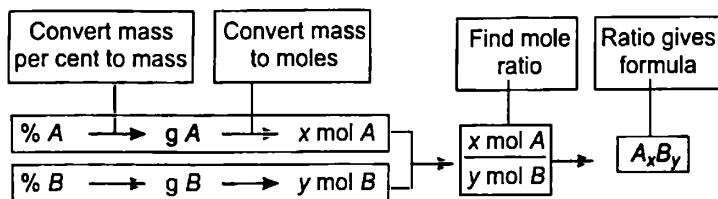


**Illustration 1** What is simplest formula of a salt that contains 40% calcium, 12% carbon and 48% oxygen?

**Solution**

| Element | Relative mass | Atomic weight (At. wt.) | Relative number of atoms | Divide by smallest number | Smallest whole number ratio of atoms |
|---------|---------------|-------------------------|--------------------------|---------------------------|--------------------------------------|
| Ca      | 40.0          | 40.0                    | $\frac{40}{40} = 1.0$    | $\frac{1}{1} = 1$ (Ca)    | 1                                    |
| C       | 12.0          | 12.0                    | $\frac{12}{12} = 1.0$    | $\frac{1}{1} = 1$ (C)     | 1                                    |
| O       | 48.0          | 16.0                    | $\frac{48}{16} = 3.0$    | $\frac{3}{1} = 3$ (O)     | 3                                    |

Thus, simplest formula = **CaCO<sub>3</sub>**

**Illustration 2** Glucose or blood sugar has the molecular formula C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>. What is the empirical formula and what is the per cent composition of glucose?

**Solution** Molecular formula : C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>

Mol ratio of C H O  
6 12 6

simplest mol ratio 1 2 3

hence, empirical formula = **CH<sub>2</sub>O**

mass of 1 mole glucose =  $12 \times 6 + 1 \times 12 + 16 \times 6$   
= 180 g mol<sup>-1</sup>

% of carbon =  $\frac{12 \times 6}{180} \times 100 = 40.0\%$

% of hydrogen =  $\frac{1 \times 12}{180} \times 100 = 6.67\%$

**Table 1.3 A Summary of Terms Used**

| Term                                         | Definition or usage                                                                                                                                                                                                                                                                              |
|----------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Atomic weight standard                       | An atomic weight of 12.00000 is arbitrarily assigned to $^{12}_6\text{C}$ .                                                                                                                                                                                                                      |
| Isotopic mass (nuclidic mass)                | The mass, in atomic mass units, u, of a single atom, on a scale in which the mass of an atom of $^{12}_6\text{C}$ is arbitrarily defined as 12.00000 u (e.g., $^{35}_{17}\text{Cl}$ has an isotopic mass of 34.968852 u).                                                                        |
| Atomic weight (relative atomic weight)       | A dimensionless (pure) number that expresses the mass of the naturally occurring mixture of isotopes of an element, relative to an arbitrarily assigned atomic weight of 12.00000 for carbon-12. These are the values listed in a table of atomic weights (e.g., atomic weight of Cl = 35.4527). |
| Formula weight (relative formula weight)     | A dimensionless (pure) number that expresses the mass of a formula unit of a compound, relative to the atomic weight standard, carbon-12 (e.g., formula weight of NaCl = 58.44). Tabulated atomic weights are used in computing formula weights.                                                 |
| Molecular weight (relative molecular weight) | A dimensionless (pure) number that compares the mass of a molecule to the atomic weight standard, carbon-12 (e.g., molecular weight of CCl <sub>4</sub> = 153.82). Tabulated atomic weights are used in computing molecular weights.                                                             |
| Mole                                         | An amount of substance containing the same number of elementary units ( $6.02214 \times 10^{23}$ ) as there are $^{12}_6\text{C}$ atoms in 12.00000 g $^{12}_6\text{C}$ .                                                                                                                        |
| Molar mass (molar weight, mole weight)       | The mass of one mole of a substance, whether the substance is composed of individual atoms (e.g., 35.45 g Cl/mol Cl), formula units (e.g., 58.44 g NaCl/mol NaCl), or molecules (e.g., 153.82 g CCl <sub>4</sub> /mol CCl <sub>4</sub> ).                                                        |

\*Where ever the term "weight" occurs, the term "mass" is equally (or even more) appropriate, e.g., atomic weight = atomic mass.

$$\% \text{ of oxygen} = \frac{16 \times 6}{180} \times 100 = 53.33\%$$

**Illustration 3** Analysis of a pure compound of an oxide of sulphur gave 50.1% sulphur and 49.9% oxygen by mass. What is the simplest formula of the compound?

**Solution**

| Element | Relative mass | Atomic weight (At. wt.) | Relative Number of atoms (Divide by At. wt.) | Divide by smallest number   | Smallest whole number ratio of atom |
|---------|---------------|-------------------------|----------------------------------------------|-----------------------------|-------------------------------------|
| S       | 50.1          | 32.1                    | $\frac{50.1}{32.1} = 1.56$                   | $\frac{1.56}{1.56} = 1$ (S) | 1                                   |
| O       | 49.9          | 16.0                    | $\frac{49.9}{16.0} = 3.12$                   | $\frac{3.12}{1.56} = 2$ (O) | 2                                   |

Thus, simplest formula = **SO<sub>2</sub>**

### Problem Solving TiPs

(Known common fractions in decimal form)

As Illustration (1) illustrates, sometimes we must convert a fraction to a whole number by multiplication by the correct integer. But we must first recognise which fraction is represented by a non-zero part of a number. The decimal equivalents of the following fractions may be useful.

| Fraction | Decimal equivalent (to 2 places) | To convert to integer multiply by |
|----------|----------------------------------|-----------------------------------|
| 1/2      | 0.50                             | 2                                 |
| 1/3      | 0.33                             | 3                                 |
| 2/3      | 0.67                             | 3                                 |
| 1/4      | 0.25                             | 4                                 |
| 3/4      | 0.75                             | 4                                 |
| 1/5      | 0.20                             | 5                                 |
| 2/5      | 0.40                             | 5                                 |
| 3/5      | 0.60                             | 5                                 |
| 4/5      | 0.80                             | 5                                 |

## Practice Exercise 2

- Write the atomic masses of the following in amu.
  - ${}_{11}^{23}\text{Na}$
  - ${}_{6}^{14}\text{C}$
  - ${}_{7}^{14}\text{N}$
  - ${}_{13}^{27}\text{Al}$
  - ${}_{12}\text{Mg}^{2+}$  containing 10 electrons
  - ${}_{8}\text{O}^{2-}$  containing 10 electrons
- Which is heavier in each pair?
  - 1 amu of  ${}^{12}\text{C}$  or 1 amu of  ${}^{13}\text{C}$
  - 1 mol of  ${}_{11}^{23}\text{Na}$  or 1 mol of  ${}_{11}^{24}\text{Na}$
  - 0.5 mol of  ${}_{2}^4\text{He}$  or 1 mol of  ${}_{1}^2\text{H}$
- The "lead" in lead pencils is actually almost pure carbon and the mass of a period mark made by a lead pencil is about 0.0001 g. How many carbon atoms are in the period?
- A binary compound of zinc and sulphur contains 67.1% zinc by mass. What is the ratio of zinc and sulphur atoms in the compound? ( $\text{Zn} = 65$ ;  $\text{S} = 32$ )
- What is the empirical formula and what is the per cent composition of dimethylhydrazine,  $\text{C}_2\text{H}_8\text{N}_2$ , a colourless liquid used as a rocket fuel?
- What is the empirical formula of an ingredient in bufferin tablets that has the per cent composition?  
C : 14.25% O : 56.93%, Mg : 28.83% by mass
- Convert the following per cent composition into molecular formulae:
  - Diborane H : 21.86%, B : 78.14%,  
Mol. wt. :  $28 \text{ g mol}^{-1}$
  - Trioxan C : 40.00%, H : 6.71%,  
O : 53.28%, Mol wt. :  $90 \text{ g mol}^{-1}$
- $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$  has 8.20 per cent Al by mass. Calculate value of  $x$ .
- Select correct alternate. Only one alternate is correct.
  - If the equivalent weight of an element is 32, then the percentage of oxygen in its oxide is
    - 16
    - 40
    - 32
    - 20
  - A hydrocarbon has 3 g carbon per gram of hydrogen, hence simplest formula is
    - $\text{CH}_4$
    - $\text{C}_6\text{H}_6$
    - $\text{C}_3\text{H}_8$
    - $\text{CH}_2$
  - Molar ratio of  $\text{Na}_2\text{SO}_3$  and  $\text{H}_2\text{O}$  is 1 : 7 in  $\text{Na}_2\text{SO}_3 \cdot x\text{H}_2\text{O}$ . Hence, mass percentage is
    - 12.5 : 87.5
    - 87.5 : 12.5
    - 50 : 50
    - 75 : 25

## Answers

- (a) 23 amu (b) 14 amu (c) 14 amu (d) 27 amu  
(e) 24 amu (f) 16 amu
- (a) 1 amu of  ${}^{13}\text{C}$  (b) 1 mol of  ${}_{11}^{24}\text{Na}$  (c) equal mass
- $5.018 \times 10^{18}$  atoms
- Zn : S :: 1 : 1
- Empirical formula :  $\text{CH}_4\text{N}$ , C : 40%, H : 13.3%, N : 46.7%
- $\text{CO}_3\text{Mg}$  7. (a)  $\text{B}_2\text{H}_6$  (b)  $\text{C}_3\text{H}_6\text{O}_3$  8.  $x = 18$
- A. (d) B. (a) C. (c)

# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** Analysis of chlorophyll shows that it contains 2.68 per cent magnesium. How many atoms of magnesium does 100 g of chlorophyll contain?

*Plan* First we determine moles of magnesium in 1 g of chlorophyll and

$$\text{number of Mg atoms} = \text{mol} \times N_0$$

**Solution** Mg in chlorophyll is 2.68%

$$\begin{aligned} \text{Thus, } 100 \text{ g chlorophyll} &= 100 \times \frac{2.68}{100} \text{ g Mg} \\ &= \frac{2.68}{24} \text{ mol Mg} \\ &= \frac{2.68 N_0}{24} \text{ atoms of Mg} \\ &= \frac{2.68 \times 6.022 \times 10^{23}}{24} \\ &= 6.7246 \times 10^{22} \text{ atoms} \end{aligned}$$

**Problem 2.** Carbohydrates are compounds containing carbon, hydrogen and oxygen in which the hydrogen to oxygen ratio is 2 : 1. A certain carbohydrate contains 40% carbon by mass. Derive molecular formula of the compound if molar mass is  $180 \text{ g mol}^{-1}$ .

*Plan* Molar ratio of hydrogen and oxygen and mass per cent of carbon have been given. Molecular weight and molecular formula are thus derived.

**Solution** Let carbohydrate be  $\text{C}_x(\text{H}_2\text{O})_y$  where  $x$  and  $y$  are whole numbers.

$$\therefore 12x + 18y = 180$$

Also 180 g of the carbohydrate has =  $12x$  carbon

$$\therefore 100 \text{ g of the carbohydrate has} \\ = \frac{12x \times 100}{180} \% \text{ carbon}$$

$$\therefore \frac{1200x}{180} = 40$$

$$\therefore x = 6$$

$$\therefore 12 \times 6 + 18y = 180$$

$$\therefore y = 6$$

$$\therefore \text{Carbohydrate is } \text{C}_x(\text{H}_2\text{O})_y = \text{C}_6(\text{H}_2\text{O})_6 \\ = \text{C}_6\text{H}_{12}\text{O}_6$$

**Problem 3.** Myoglobin stores oxygen for metabolic processes in muscle. Chemical analysis shows that it contains 0.34% Fe by mass. What is the molar mass of myoglobin? (There is one Fe atom per molecule).

*Plan* Every myoglobin molecule has one Fe atom. Every 100 g of it has 0.34 g Fe hence, molar mass of myoglobin containing 56 g Fe per mol can be determined.

**Solution** If 0.34 g Fe is present then myoglobin

$$= 100 \text{ g}$$

$$\text{If 56 g of Fe is present then myoglobin} = \frac{100}{0.34} \times 56$$

$$= 16470.6 \text{ g mol}^{-1}$$

**Problem 4.** A compound X contains 63.3 per cent manganese (Mn) and 36.7 per cent oxygen by mass. When X is heated, oxygen gas is evolved and a new compound Y containing 72.0 per cent Mn and 28.0 per cent O is formed. (a) Determine the empirical formula of X and Y. (b) Write a balanced equation for the conversion of X to Y. (Mn = 55, O = 16)

*Plan* From the percentage of Mn and O, empirical formula of X and Y are derived.

**Solution** For the compound X

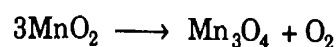
|    | %    | $\text{mol} = \frac{\%}{\text{atomic mass}}$ | Simplest ratio |
|----|------|----------------------------------------------|----------------|
| Mn | 63.3 | 1.15                                         | 1              |
| O  | 36.7 | 2.29                                         | 2              |

Empirical formula :  $\text{MnO}_2$

For the compound Y

|    | %    | $\text{mol} = \frac{\%}{\text{atomic mass}}$ | Simplest ratio | Whole number ratio |
|----|------|----------------------------------------------|----------------|--------------------|
| Mn | 72.0 | 1.31                                         | 1              | 3                  |
| O  | 28.0 | 1.75                                         | 1.33           | 4                  |

Empirical formula :  $\text{Mn}_3\text{O}_4$



**Problem 5.** Ferrocene, a substance proposed for use as a gasoline additive, has the per cent composition 5.42% H, 64.56% C, and 30.02% Fe. What is the empirical formula of ferrocene?

**Plan** Per cent composition is to be converted to moles, then to molar ratio and then into integral mole ratio (if it is fraction).

**Solution**

| Element          | %     | Mol = $\frac{\%}{\text{atomic mass}}$ | mole ratio |
|------------------|-------|---------------------------------------|------------|
| $^{12}\text{C}$  | 64.56 | 5.38                                  | 10         |
| $^1\text{H}$     | 5.42  | 5.42                                  | 10         |
| $^{56}\text{Fe}$ | 30.02 | 0.54                                  | 1          |

Empirical formula is  $\text{C}_{10}\text{H}_{10}\text{Fe}$ .

**Problem 5.** Phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is a colourless, syrupy liquid used in detergents, fertilizer, tooth pastes, and in carbonated beverages for a “tangy” flavour. Calculate the per cent composition by mass of H, P and O in this compound. (H = 1, P = 31, O = 16)

**Plan** In one mole (= 98 g) amounts of H, P and O are known, hence their mass per cent can be calculated.

**Solution** One mole of  $\text{H}_3\text{PO}_4 = 1 \text{ mole} \times 98 \text{ g mol}^{-1} = 98 \text{ g}$   
 H present in one mole = 3 g  
 $\therefore$  % of H in  $\text{H}_3\text{PO}_4 = \frac{3}{98} \times 100 = 3.06\%$

P present in one mole = 31 g

$$\therefore \% \text{ of P in } \text{H}_3\text{PO}_4 = \frac{31}{98} \times 100 = 31.63\%$$

O present in one mole = 64 g

$$\therefore \% \text{ of O in one mole} = \frac{64}{98} \times 100 = 65.31\%$$

**Problem 7.** What is the ratio of the masses of oxygen that are combined with 1.08 g of nitrogen in the compounds  $\text{N}_2\text{O}_3$  and NO?

**Plan** First we calculate the mass of O that combines with one gram of N in each compound. Then we determine the ratio of the values of  $\frac{\text{g(O)}}{\text{g(N)}}$  for two compounds.

**Solution** In  $\text{N}_2\text{O}_3$ :  $\frac{? \text{ g(O)}}{\text{g(N)}} = \frac{48.0 \text{ g(O)}}{28.0 \text{ g(N)}} = \frac{1.71 \text{ g(O)}}{\text{g(N)}}$

In NO:  $\frac{? \text{ g(O)}}{\text{gN}} = \frac{16. \text{ g(O)}}{14.0 \text{ g(N)}} = \frac{1.14 \text{ g(O)}}{\text{g(N)}}$

The ratio is  $\frac{\text{g(O)}}{\text{g(N)}}$  in ( $\text{N}_2\text{O}_3$ )

$$\frac{1.71 \text{ g(O)} / \text{g(N)}}{1.14 \text{ g(O)} / \text{g(N)}} = \frac{1.5}{1.0} = \frac{3}{2}$$

$\frac{\text{g(O)}}{\text{g(N)}}$  in (NO)

Thus, we observe that the ratio is 3 mass units g(O) in ( $\text{N}_2\text{O}_3$ ) to 2 mass units of O (in NO or  $\text{N}_2\text{O}_2$ ). This represents law of multiple proportions.

# Master Exercises

## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

1. What is the name of the following process?  
gas  $\longrightarrow$  solid
2. What is the valency of carbonate if its equivalent weight is  $30 \text{ g equiv}^{-1}$ ?
3. 24 g of magnesium combines with oxygen forming 40 g of oxide. What is equivalent weight of magnesium?
4. 27 g of aluminium combines with hydrogen forming 30 g of hydride. What is equivalent weight of aluminium?
5.  $\text{H}_3\text{PO}_2$  only forms  $\text{NaH}_2\text{PO}_2$ . What is its equivalent weight of acid?
6.  $\text{H}_3\text{PO}_3$  forms  $\text{NaH}_2\text{HPO}_3$  and  $\text{Na}_2\text{HPO}_3$ . What is equivalent weight of acid at each stage of salt formation?
7.  $\text{H}_3\text{PO}_4$  forms  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$  and  $\text{Na}_3\text{PO}_4$ . What is equivalent weight of acid at each stage of salt formation?
8. When a piece of sulphur is burnt in air, it disappears. How could you prove that it is not destroyed?
9. Taking VD of hydrogen as 1, determine  
(a) VD of  $\text{CH}_4$                       (b) VD of  $\text{O}_2$   
(c) VD of  $\text{CO}_2$
10. Calculate number of equivalents in  
(a) 1.6 g  $\text{O}_2$  gas                      (b) 0.49 g  $\text{H}_2\text{SO}_4$   
(c) 1.80 g  $\text{H}_2\text{O}$                       (d) 1.6 g  $\text{CH}_4$
11. Calculate equivalent weights of the underlined based on following reaction : (Take molecular weight =  $M$ )  
(a)  $\underline{\text{N}_2} + 3\text{H}_2 \longrightarrow 2\underline{\text{NH}_3}$   
(b)  $\text{Ca}(\text{OH})_2 + \underline{\text{H}_3\text{PO}_4} \longrightarrow \text{CaHPO}_4$   
(c)  $\underline{\text{Zn}} + \text{H}_2\text{SO}_4 \longrightarrow \text{ZnSO}_4 + \text{H}_2$   
(d)  $2\underline{\text{FeSO}_4} + \text{H}_2\text{SO}_4 + \text{O} \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$

12. What is the relation between specific heat and atomic weight?
13. The specific heat of a metal  $M$  is 0.25. Its equivalent weight is 12.  
(a) What is its atomic weight?  
(b) What is the formulas of its (i) chloride, (ii) sulphate and (iii) phosphate?
14. Calculate number of moles and atoms of each in 1.8 g  $\text{C}_6\text{H}_{12}\text{O}_6$ .

### Analytical Questions

#### Law of Chemical Combination

1. Benzene, ethane and ethylene are just three of a large number of hydrocarbons—compounds that contain only carbon and hydrogen. Show how the following data are consistent with the law of multiple proportions.

| Compound | Mass of carbon in 5.00 g sample | Mass of hydrogen in 5.00 g sample |
|----------|---------------------------------|-----------------------------------|
| Benzene  | 4.61 g                          | 0.39 g                            |
| Ethane   | 4.00 g                          | 1.00 g                            |
| Ethylene | 4.29 g                          | 0.71 g                            |

2. Ammonia,  $\text{NH}_3$  and hydrazine,  $\text{N}_2\text{H}_4$ , are both binary compounds of nitrogen and hydrogen. Based on the law of multiple proportions, how many grams of hydrogen would you expect 2.34 g of nitrogen to combine with to yield ammonia? To yield hydrazine.
3. If 3.670 g of nitrogen combine with 0.5275 g of hydrogen to yield compound X, how many grams of nitrogen would combine with 1.575 g of hydrogen to make the same compound? Is X ammonia or hydrazine?

**Mole**

4. The table below gives number of electrons, protons and neutrons in atoms or ions of a number of elements. Answer the following :

| Atom or Ion of element | A | B  | C  | D  | E  | F | G  |
|------------------------|---|----|----|----|----|---|----|
| Number of electrons    | 5 | 10 | 18 | 28 | 36 | 5 | 9  |
| Number of protons      | 5 | 7  | 19 | 30 | 35 | 5 | 9  |
| Number of neutrons     | 5 | 7  | 20 | 36 | 46 | 6 | 10 |

- Which of the species are neutral?
  - Which are negatively charged?
  - Which are positively charged?
  - What are the conventional symbols for all the species?
5. The carat is the unit of mass used by jewellers. One carat is exactly 200 mg. How many carbon atoms are present in a 24 carat diamond?
6. The natural abundance of the two stable isotopes of hydrogen (hydrogen and deuterium) are  ${}^1_1\text{H}$ : 99.985% and  ${}^2_1\text{H}$ : 0.015%. Assume that water exists as either  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$ . Calculate the number of  $\text{D}_2\text{O}$  molecules in exactly 400 mL water. (Density =  $1.00 \text{ g mL}^{-1}$ )
7. A solution containing 10.0 millimol of  $\text{CaCl}_2$  is diluted to 1 L. Calculate the number of grams of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  per mL of final solution.

**Percentage Composition and Empirical Formula**

8. All of the substance listed below are fertilizers that contribute nitrogen to the soil. Which of these is the richest source of nitrogen on a mass percentage basis?
- Urea,  $(\text{NH}_2)_2\text{CO}$
  - Ammonium nitrate,  $\text{NH}_4\text{NO}_3$
  - Guanidine,  $\text{HNC}(\text{NH}_2)_2$
  - Ammonia,  $\text{NH}_3$
9. The aluminium sulphate hydrate  $[\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}]$  contains 8.20 per cent Al by mass. Calculate  $x$ , that is, the number of water molecules associated with each  $\text{Al}_2(\text{SO}_4)_3$  units.
10. Calculate the per cent composition by mass of all the elements in calcium phosphate  $\text{Ca}_3(\text{PO}_4)_2$ .
11. Platinum forms two different compounds with chlorine. One contains 26.7 per cent Cl by mass, and the other contains 42.1 per cent Cl by mass. Determine the empirical formulae of the two compounds. (Pt = 195)

12. Disilane,  $\text{Si}_2\text{H}_x$ , is analysed and found to contain 90.28% by weight silicon. What is the value of  $x$ ? (Si = 28)
13. Cytochrome C is an iron-containing enzyme found in the cells of all aerobic organisms. If cytochrome C is 0.43% Fe by weight, what is its minimum molecular weight?
14. What is empirical formula of stannous fluoride, a compound added to tooth paste to protect teeth against decay? Its mass per cent composition is 24.25% F, 75.75% Sn.
15. Analysis of a metal chloride  $\text{XCl}_3$  shows that it contains 67.2% Cl by mass. Calculate the molar mass of X and identify the element.
16. A sample of a compound of nitrogen (N) and oxygen (O) contains 1.52 g of N and 3.47 g of O. The molar mass of this compound is known to be between 90 g and 95 g. Determine the molecular formula and molar mass of this compound. (N = 14, O = 16)

**NCERT Problems**

- Calculate the molar mass of
  - $\text{H}_2\text{O}$
  - $\text{CO}_2$
  - $\text{CH}_4$
- Determine the empirical formula of an oxide of iron which has 69.9% iron and 30.1% oxygen (Fe = 55.85 amu; O = 16.00 amu).
- How much copper can be obtained from 100 g of anhydrous copper sulphate ( $\text{CuSO}_4$ )? Cu = 63.5; S = 32, O = 16 (all in amu).
- Calculate the following in three moles of ethane gas ( $\text{C}_2\text{H}_6$ )
  - moles of carbon atoms
  - moles of hydrogen atoms
  - molecules of ethane
- Which one of the following will have largest number of atoms? [Au = 197, Na = 23, Li = 7, Cl = 35.5 in amu]
  - 1g Au(s)
  - 1g Na(s)
  - 1g Li(s)
  - 1g  $\text{Cl}_2$ (g)
- What will be the mass of one  ${}^{12}\text{C}$  atom in gram?
- Calculate the number of atoms in each of the following :
  - 52 moles He
  - 52 u of He
  - 52 g He



## Exercise 2

### (Stage 2 : High Skill Problem Solving)

#### Only One Option Correct

- In which of the following pairs do the two species resemble each other most closely in chemical properties?
  - ${}^1_1\text{H}$  and  ${}^2_1\text{H}$
  - ${}^{16}_8\text{O}$  and  ${}^{16}_8\text{O}^{2-}$
  - ${}^{24}_{12}\text{Mg}$  and  ${}^{24}_{12}\text{Mg}^{2+}$
  - ${}^{14}_7\text{N}$  and  ${}^{14}_7\text{N}^{3-}$
- One isotope of a non-metallic element has mass number 127 and 74 neutrons in the nucleus. The anion derived from the isotope has 54 electrons. Hence, symbol for the anion is
  - ${}^{127}_{54}\text{X}^-$
  - ${}^{127}_{53}\text{X}^-$
  - ${}^{74}_{53}\text{X}^-$
  - ${}^{74}_{54}\text{X}^-$
- Which of the following is the richest source of ammonia on a mass percentage basis?
  - $\text{NH}_4\text{NO}_3$
  - $\text{NH}_2\text{CONH}_2$
  - $\text{NH}_3$
  - $\text{HNC}(\text{NH}_2)_2$
- Which of the following substances contains greatest mass of chlorine?
  - 5.0 g  $\text{Cl}_2$
  - 0.5 mol  $\text{Cl}_2$
  - 0.10 mol  $\text{KCl}$
  - 30.0 g  $\text{MgCl}_2$
- When 0.273 g of  $\text{Mg}$  is heated strongly in a nitrogen ( $\text{N}_2$ ) atmosphere, 0.378 g of the compound is formed. Hence, compound formed is
  - $\text{Mg}_3\text{N}_2$
  - $\text{Mg}_3\text{N}$
  - $\text{Mg}_2\text{N}_3$
  - $\text{MgN}$
- A certain metal sulphide,  $\text{MS}_2$ , is used extensively as a high temperature lubricant. If  $\text{MS}_2$  is 40.06% by mass sulphur, metal  $M$  has atomic mass
  - 160 amu
  - 64 amu
  - 40 amu
  - 96 amu
- The molar mass of a compound if 0.372 mol of it has a mass of 186 g is
  - 200 g
  - 372 g
  - 500 g
  - 186 g
- Which of the following has maximum number of C atoms?
  - 4.4 g  $\text{CO}_2$
  - 3.0 g  $\text{C}_2\text{H}_6$
  - 4.4 g  $\text{C}_3\text{H}_8$
  - 1.3 g  $\text{C}_6\text{H}_6$
- Number of atoms present in 1.8 g  $\text{H}_2\text{O}$ , 1.7 g  $\text{NH}_3$  and 1.6 g  $\text{CH}_4$ , in the increasing order is
  - $\text{H}_2\text{O} < \text{NH}_3 < \text{CH}_4$
  - $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O}$
  - $\text{CH}_4 = \text{NH}_3 = \text{H}_2\text{O}$
  - $\text{NH}_3 < \text{CH}_3 < \text{H}_2\text{O}$
- Number of atoms in 20 g  $\text{Ca}$  is equal to number of atoms is
  - 20 g  $\text{Mg}$
  - 1.6 g  $\text{CH}_4$
  - 1.8 g  $\text{H}_2\text{O}$
  - 1.7 g  $\text{NH}_3$
- $\text{Na}_2\text{SO}_3 \cdot x\text{H}_2\text{O}$  has 50%  $\text{H}_2\text{O}$  by mass. Hence,  $x$  is
  - 4
  - 5
  - 6
  - 7
- Mass of one atom of  $X$  is  $6.66 \times 10^{-23}$  g. Hence, number of mole of atom  $X$  in 40 kg is
  - $10^3$  mol
  - $10^{-3}$  mol
  - $\frac{40 \times 10^3}{6.66 \times 10^{-23}}$  mol
  - $\frac{40 \times 10^3}{6.022 \times 10^{23}}$  mol
- To make 0.01 mol, which of the following has maximum mass?
  - $\text{NaHCO}_3$
  - $\text{Na}_2\text{CO}_3$
  - $\text{Na}_2\text{SO}_4$
  - $\text{Na}_2\text{C}_2\text{O}_4$
- In a glass-tube, there is 18 g of glucose. 0.08 mol of glucose is taken. Glucose left in the glass-tube is
  - 0.10 g
  - 17.92 g
  - 3.60 mol
  - 3.60 g
- Rest mass of an electron is  $9.11 \times 10^{-31}$  kg. Molar mass of the electron is
  - $1.50 \times 10^{-31}$  kg mol $^{-1}$
  - $9.11 \times 10^{-31}$  kg mol $^{-1}$
  - $5.5 \times 10^{-7}$  kg mol $^{-1}$
  - $6.02 \times 10^{23}$  kg mol $^{-1}$
- A sample of ammonium phosphate  $(\text{NH}_4)_3\text{PO}_4$  contains 3.18 moles of H atoms. The number of moles of O atoms in the sample is
  - 0.265
  - 0.795
  - 1.06
  - 3.18
- A sample of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  contains 3.782 g of Cu. How many grams of oxygen are in this sample? ( $\text{Cu} = 63.5$ )
  - 0.952 g
  - 3.80 g
  - 4.761 g
  - 8.576 g
- Cortisone is a molecular substance containing 21 atoms of carbon per molecule. The mass percentage of carbon in cortisone is 69.98%. Its molar mass is
  - 176.5
  - 252.2
  - 287.6
  - 360.1
- In a hydrocarbon C is 3 g per g of hydrogen. Hence, hydrocarbon is
  - $\text{CH}_4$
  - $\text{C}_2\text{H}_6$
  - $\text{C}_3\text{H}_8$
  - $\text{C}_4\text{H}_{10}$
- Which has maximum percentage of Cl?
  - $\text{C}_6\text{H}_6\text{Cl}_6$
  - $\text{CHCl}_3$
  - $\text{C}_6\text{H}_5\text{Cl}$
  - $\text{CH}_3\text{Cl}$
- A spherical ball of radius 7 cm contains 56% iron. If density is 1.4 g/cm $^3$ , number of moles of Fe present approximately is
  - 10
  - 15
  - 20
  - 25

22. In the following final result is ... 0.1 mol  $\text{CH}_4 + 3.01 \times 10^{23}$  molecules  $\text{CH}_4 - 9.6 \text{ g CH}_4 = x \text{ mol H atoms}$   
 (a) 0 mol H atom (b) 0.2 mol H atom  
 (c) 0.3 mol H atom (d) 0.4 mol H atom
23. If we assume that  $N_0 = 1.2 \times 10^{23} \text{ mol}^{-1}$ , then molar mass of  $\text{O}_2$  will be taken as  
 (a)  $32 \text{ g mol}^{-1}$  (b)  $\frac{32}{6} \text{ g mol}^{-1}$   
 (c)  $32 \times 10^{23} \text{ g mol}^{-1}$  (d)  $\frac{1 \times 10^{23}}{32} \text{ g mol}^{-1}$
24.  $\text{CO}, \text{CO}_2, \text{C}_2\text{O}_3$  follow  
 (a) law of definite proportion  
 (b) law of multiple proportion  
 (c) law of conservation of mass  
 (d) all of the above
25. In a gas S and O are 50% by mass, hence, their mol ratio is  
 (a) 1 : 1 (b) 1 : 2  
 (c) 2 : 1 (d) 3 : 1
- (b) 46 g  $\text{CaCl}_2$  would contain the same number of chloride ions as are contained in 48.6 g  $\text{NaCl}$   
 (c) 17 g  $\text{NH}_3$  would contain the same volume of  $\text{H}_2$  at NTP as are contained in 18 g  $\text{H}_2\text{O}$  at NTP  
 (d) 1 mole  $\text{CO}$  would combine with same mole of  $\text{O}_2$  to form  $\text{CO}_2$  as required by 1 mole of  $\text{SO}_2$  to form  $\text{SO}_3$
6. Equal mass of water is lost on heating of 1 mole of each of  
 (a)  $\text{NaHCO}_3$  (b)  $\text{Ca}(\text{HCO}_3)_2$   
 (c)  $\text{KHCO}_3$  (d)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
7. Empirical formula will be same in with following compounds  
 (a)  $\text{CH}_3\text{CO}_2\text{H}$  (b)  $\text{C}_6(\text{H}_2\text{O})_6$   
 (c)  $\text{HCHO}$  (d)  $\text{C}_{12}(\text{H}_2\text{O})_{11}$
8. Consider following species  
 I :  $\text{CO}$ ; II :  $\text{NO}$ ;  
 III :  $\text{N}_2$ ; IV :  $\text{HCHO}$   
 Select species with equal number of neutrons, protons and electrons in each.  
 (a)  $\text{CO}, \text{N}_2$  (b)  $\text{CO}, \text{HCHO}$   
 (c)  $\text{NO}, \text{HCHO}$  (d)  $\text{N}_2, \text{NO}, \text{CO}$
9. Which of the following may contain two neutrons and two protons?  
 (a) He (b)  $\text{D}_2$   
 (c)  $\text{He}_2^{2+}$  (d)  $\text{H}_2$
10.  $^{12}_6\text{C}$  and  $^{14}_6\text{C}$  resemble in  
 (a) number of protons (b) number of electrons  
 (c) number of neutrons (d) chemical properties

### One or More Than One Options Correct

1. Equal moles of the substance are present in  
 (a) 1.6 g  $\text{CH}_4$  (b) 1.7 g  $\text{NH}_3$   
 (c) 1.8 g  $\text{H}_2\text{O}$  (d) 1.2 g  $\text{Mg}$
2. In which cases law of conservation of mass are followed?  
 (a) 10 g  $\text{CaCO}_3$  on heating gives 0.1 mole  $\text{CaO}$  and 2.24 L  $\text{CO}_2$  at NTP  
 (b) 1 mole  $\text{N}_2$  and 1 mole  $\text{H}_2$  combine to form 2 moles of  $\text{NH}_3$   
 (c) 0.2 mole  $\text{SO}_2$  combines with 3.2 g  $\text{O}_2$  to form 0.2 mole  $\text{SO}_3$   
 (d) 1 g  $\text{H}_2$  combines with 0.5 g  $\text{O}_2$  to form 1.5 g  $\text{H}_2\text{O}$
3. One formula unit of a substance (underlined) is present in each of  
 (a) 200 g  $\text{CaCO}_3$  with 50% impurity  
 (b) 38 g  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  with 1 mole  $\text{D}_2\text{O}$   
 (c) 360 g  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  and  $\text{C}_6\text{H}_{12}\text{O}_6$  with 0.1 mole  $\text{C}_6\text{H}_{12}\text{O}_6$   
 (d) 46 g  $\text{N}_2\text{H}_4\text{CO}$  with 60% purity
4. Which represents one mole?  
 (a) 22.4 L He at STP  
 (b) 16 g  $\text{O}_2$   
 (c) 158 g  $\text{KMnO}_4$   
 (d) 392 g  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
5. Select correct alternate(s).  
 (a) 23.5 g  $\text{SO}_2$  would contain the same mass of oxygen as is contained in 33.7 g of  $\text{As}_2\text{O}_5$  ( $\text{As} = 75$ )

### Brain Twisters

1. What is equivalent weight of  $\text{H}_3\text{O}^+$ ?
2. Equivalent weight of  
 (a)  $\text{H}_3\text{PO}_2 = \frac{\text{molecular weight}}{1}$   
 (b)  $\text{H}_3\text{PO}_2 = \frac{\text{molecular weight}}{2}$   
 (c)  $\text{H}_3\text{PO}_3 = \frac{\text{molecular weight}}{3}$   
 Explain the difference.
3. Determine equivalent weight of carbon in the following :  
 (a)  $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$   
 (b)  $\text{C} + 2\text{H}_2 \longrightarrow \text{CH}_4$   
 (c)  $2\text{C} + \text{H}_2 \longrightarrow \text{C}_2\text{H}_2$   
 (d)  $2\text{C} + 2\text{H}_2 \longrightarrow \text{C}_2\text{H}_4$   
 (e)  $2\text{C} + 3\text{H}_2 \longrightarrow \text{C}_2\text{H}_6$   
 (f)  $3\text{C} + 4\text{H}_2 \longrightarrow \text{C}_3\text{H}_8$

What do you conclude about equivalent weight?

- Equivalent weight of two oxides A and B of sulphur are 16 and 13.33 g equivalent<sup>-1</sup> respectively. What are these oxides?
- Equivalent weights of two hydrides of nitrogen are 5.66 and 8. Derive formulae of hydride.
- A solution contains 200 g ppm CaCO<sub>3</sub>. Express this concentration in
  - millimoles per gram
  - number of CaCO<sub>3</sub> molecules per gram
- How many carbon atoms are present in a diamond weighing 200 mg and of 20 carat purity?
- 100 g of ethyl alcohol-water mixture contains 1 mole of ethyl alcohol. What is molar ratio of ethyl alcohol and water in the mixture?
- Students A and B derived equivalent weights of KHC<sub>2</sub>O<sub>4</sub> quite different. Explain.
- 0.24 g of magnesium was burnt in the atmosphere of oxygen when residue formed weighed 0.40 g. Derive equivalent weight of magnesium.
- Cost of a fertilizer is based on the percentage of nitrogen in it. Which of the fertilizers should be priced maximum?
  - NH<sub>4</sub>NO<sub>3</sub>
  - NH<sub>2</sub>CONH<sub>2</sub>
  - KNO<sub>3</sub>
  - NH<sub>4</sub>Cl
- One equivalent of calcium phosphate Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is dissolved in HCl
 
$$\text{Ca}_3(\text{PO}_4)_2 + 6\text{HCl} \longrightarrow 3\text{CaCl}_2 + 2\text{H}_3\text{PO}_4$$
  - How many moles of CaCl<sub>2</sub> are formed?
  - How many moles of H<sub>3</sub>PO<sub>4</sub> are formed?

## Passage Comprehension Questions

### Passage 1

Study the following observations and answer the questions at the end of it.

The following is a crude but effective method for estimating the order of magnitude of Avogadro's number using stearic acid (C<sub>18</sub>H<sub>36</sub>O<sub>2</sub>). When stearic acid is added to water, its molecules collect at the surface and form a monolayer; that is, the layer is only one molecule thick. The cross-sectional area of each stearic acid molecule has been measured to be 0.21 nm<sup>2</sup>. In one experiment it is found that 1.4 × 10<sup>-4</sup> g of stearic acid is needed to form a monolayer over water in a dish of diameter 20 cm. (the area of a circle of radius *r* is π*r*<sup>2</sup>.)

- Based on these measurements value of Avogadro's number is
  - 3 × 10<sup>23</sup>
  - 6 × 10<sup>23</sup>
  - 4 × 10<sup>23</sup>
  - 1 × 10<sup>23</sup>
- What is equivalent of 1g H in amu for this value of Avogadro's number?
  - 1.66 × 10<sup>-24</sup> g
  - 3.33 × 10<sup>-24</sup> g
  - 2.5 × 10<sup>-24</sup> g
  - 1 × 10<sup>-23</sup> g

### Passage 2

Study the following passage regarding fertilizer K<sub>2</sub>O and answer the questions at the end of it.

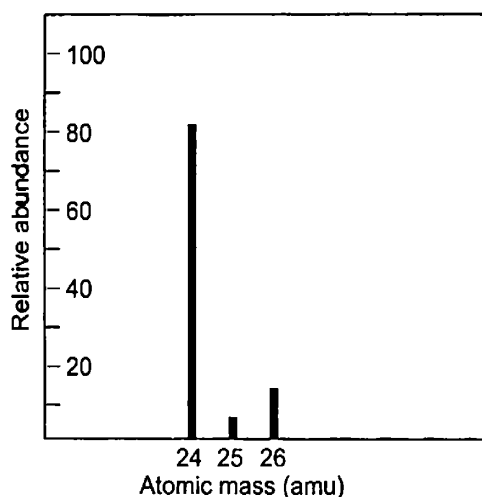
Potash is any potassium mineral that is used for its potassium content. Most of the potash produced in the United States goes into fertilizer. The major sources of potash are potassium chloride (KCl) and potassium sulphate (K<sub>2</sub>SO<sub>4</sub>). Potash production is often reported as the potassium oxide (K<sub>2</sub>O) equivalent or the amount of K<sub>2</sub>O that could be made from a given mineral. KCl costs ₹ 50 per kg.

- What is the cost of K per mol of the KCl sample?
  - ₹ 13.42 mol<sup>-1</sup>
  - ₹ 3.73 mol<sup>-1</sup>
  - ₹ 1.00 mol<sup>-1</sup>
  - ₹ 2.00 mol<sup>-1</sup>
- For what price must K<sub>2</sub>SO<sub>4</sub> be sold in order to supply the same amount of potassium as in KCl?
  - ₹ 58.40 kg<sup>-1</sup>
  - ₹ 50.00 kg<sup>-1</sup>
  - ₹ 42.82 kg<sup>-1</sup>
  - ₹ 25.00 kg<sup>-1</sup>
- What mass (in kg) of K<sub>2</sub>O contains the same number of moles of K atoms as 1.00 kg KCl?
  - 0.158 kg
  - 0.315 kg
  - 1.262 kg
  - 0.631 kg

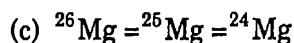
### Passage 3

Study the following observations and answer the questions at the end of it.

The mass spectrum (given below) of magnesium has three peaks, which indicates that magnesium has three isotopes. The questions given below are based on this mass spectrum.



- Which isotope has maximum number of atoms per gram of each?
  - Mg-24
  - Mg-25
  - Mg-26
  - Equal
- Number of atoms in one mole of each isotope is placed in increasing order
  - <sup>24</sup>Mg < <sup>25</sup>Mg < <sup>26</sup>Mg
  - <sup>26</sup>Mg < <sup>25</sup>Mg < <sup>24</sup>Mg



(d) given data is insufficient

3. Average atomic mass of Mg is approximately

(a) 25.0

(b) 24.3

(c) 25.2

(d) 25.8

## Assertion & Reason

Codes :

(a) Both **A** and **R** are true and **R** is the correct explanation of **A**.(b) Both **A** and **R** are true but **R** is not the correct explanation of **A**.(c) **A** is true but **R** is false.(d) **A** is false but **R** is true.1. **Assertion (A)** : When 10 g of  $\text{CaCO}_3$  is decomposed, 5.6 g of residue is left and 4.4 g of  $\text{CO}_2$  escapes.**Reason (R)** : Law of mass conservation is followed.2. **Assertion (A)** :  $\text{SO}_2$  and  $\text{SO}_3$  obey "law of multiple proportion".**Reason (R)** : Every sample of  $\text{SO}_2$  contains 1 part sulphur and 1 part oxygen by mass.3. **Assertion (A)** :  $\text{SO}_2$  from oxidation of sulphur or  $\text{H}_2\text{S}$  contains sulphur and oxygen in the mass ratio of 1 : 2.**Reason (R)** : Different samples of a pure chemical substance always contain the same proportions of elements by mass.4. **Assertion (A)** : In  $\text{Fe}^{2+}$ , there are 24 electrons and 30 neutrons and thus, ionic mass is 56.**Reason (R)** : Ionic mass = neutron + proton  
and proton = electrons in neutral species

## True & False

1. If there are 10 electrons and 8 neutrons in  $X^{2-}$ , then its ionic mass is 18.2.  $\text{SO}_2$  contains sulphur and oxygen in 1 : 1 mass ratio.3. 20 g  $\text{CaCO}_3$  (50% pure) on strongly heating gives 5.6 g residue.4. Mass of 1 mole of electrons is  $5.48 \times 10^{-7}$  kg.5. Number of atoms in 1.6 g  $\text{CH}_4$ , 1.7 g  $\text{NH}_3$  and 1.8 g  $\text{H}_2\text{O}$  are equal.6. If 1 mole of  $\text{H}_2$  is taken out from 2 g  $\text{H}_2$ , 1 g  $\text{H}_2$  is left.7. 1 amu is equal to  $1.66 \times 10^{-24}$  g.8. Out of  $\text{CH}_3\text{Cl}$ ,  $\text{C}_6\text{H}_6\text{Cl}_6$ , and  $\text{CCl}_3\text{CHO}$ , maximum percentage of chlorine is in  $\text{C}_6\text{H}_6\text{Cl}_6$ .

9. 1 ppm is equal to 1 mg per kg.

10. Equivalent mass of  $\text{NH}_3$  is 17.

## Fill in the Blanks

1. NO and  $\text{NO}_2$  follow the law of .....2.  $\text{SO}_3$  contains sulphur and oxygen in the mass ratio of .....

3. Hydrocarbon containing 4 g carbon per gram hydrogen is .....

4. If  $X^{2+}$  is isotonic (same number of neutrons) of  $\text{H}_2\text{O}$  and contains 10 electrons then ionic mass of  $X^{2+}$  is .....

5. 1 mole of barium nitrate and 1 mole of ammonium phosphate form ..... mole of barium phosphate.

6. Percentage of sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) in hydrated salt is 50. Hence, molecular formula of hydrated salt is .....

7. Concentration 1 ppm = ..... ppb.

8. Concentration 1 microgram per gram = ..... ppm.

9.  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$  and  $\text{SO}_2$  follow law of .....

10. Atomic mass unit is also called .....

## Matrix-Match Type Questions

### I. Only One Correct

1. Match % of carbon (in List I) with the compound (in List II).

| List I   | List II                           |
|----------|-----------------------------------|
| A. 20%   | 1. $\text{CH}_4$                  |
| B. 52.2% | 2. $\text{CO}_2$                  |
| C. 75%   | 3. $\text{C}_2\text{H}_6\text{O}$ |
| D. 27.3% | 4. $\text{CN}_2\text{OH}_4$       |
| E. 12%   | 5. $\text{CaCO}_3$                |

2. Match Laws of chemical combinations (in List I) with the examples followed (in List II).

| List I                          | List II                                                                                                                                                      |
|---------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|
| A. Law of conservation of mass  | 1. $\text{CH}_4$ has carbon and hydrogen in 3 : 1 mass ratio.                                                                                                |
| B. Law of multiple proportion   | 2. 10 mL $\text{N}_2$ combines with 30 mL of $\text{H}_2$ to form 20 mL of $\text{NH}_3$ .                                                                   |
| C. Law of definite proportion   | 3. S and $\text{O}_2$ combine to form $\text{SO}_2$ and $\text{SO}_3$ .                                                                                      |
| D. Law of reciprocal proportion | 4. In $\text{H}_2\text{S}$ and $\text{SO}_2$ mass ratio of H and O w.r.t. sulphur is 1 : 16, hence in $\text{H}_2\text{O}$ , mass ratio of H and O is 1 : 8. |
| E. Gay Lussac's law             | 5. 4.2 g $\text{MgCO}_3$ gives 2.0 g residue on heating.                                                                                                     |

## II. One or More Correct

1. Match the item in Column I with the compounds in Column II.

| Column I                  | Column II                                       |
|---------------------------|-------------------------------------------------|
| A. Same % of C (40%)      | 1. $\text{CH}_3\text{COOH}$                     |
| B. Same % of H (6.67%)    | 2. $\text{NH}_2\text{CONH}_2$                   |
| C. Same % of O (53.3%)    | 3. $\text{HCHO}$                                |
| D. Same empirical formula | 4. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ |
|                           | 5. $\text{HCOOCH}_3$                            |

2. Match the item in Column I with the given amount in Column II.

| Column I                 | Column II                            |
|--------------------------|--------------------------------------|
| A. 1 equivalent          | 1. 8 g oxygen (O)                    |
| B. 0.5 mole              | 2. 1 g hydrogen (H)                  |
| C. $\frac{N_0}{2}$ atoms | 3. 35.5 g chlorine ( $\text{Cl}_2$ ) |
| D. $N_0$ molecules       | 4. 66.0 g $\text{H}_3\text{PO}_2$    |
|                          | 5. 49 g $\text{H}_2\text{SO}_4$      |

## Integer Answer Types

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the ORS have to be darkened. For example, if the correct answers to question number X, Y, Z and W (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will like the following.

| X | Y | Z | W |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 1 | 1 | 1 | 1 |
| 2 | 2 | 2 | 2 |
| 3 | 3 | 3 | 3 |
| 4 | 4 | 4 | 4 |
| 5 | 5 | 5 | 5 |
| 6 | 6 | 6 | 6 |
| 7 | 7 | 7 | 7 |
| 8 | 8 | 8 | 8 |
| 9 | 9 | 9 | 9 |

## Set I

1. 1 g of hydrogen has  $x$  g of carbon in methane. This  $x$  is .....

2.  $\text{Na}_2\text{SO}_3 \cdot y\text{H}_2\text{O}$  has 50%  $\text{H}_2\text{O}$  by mass. Thus,  $y$  is .....
3. If Avogadro's number would have been  $1 \times 10^{10}$ , instead of  $6.02 \times 10^{23}$ , then mass of one atom of H would be ..... amu.
4. Sum of neutrons and electrons in  $\text{H}_2^+$  is .....
5. When neutron changes to proton, atomic number changes by ..... unit.
6. When 1 mole of  $\text{Na}_2\text{CO}_3$  is heated,  $\text{CO}_2$  lost is ..... mole.
7. Empirical formula of substance with molar mass 180 is  $\text{CH}_2\text{O}$ . Thus, ratio of molecular formula to empirical formula is .....
8. When 2.495 g of  $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$  (molar mass 249.5) is heated 0.05 mole of  $\text{H}_2\text{O}$  is lost. Thus,  $x$  is .....

## Set II

1. In Japan, radioactive water is leaking into sea from nuclear reactors (April 04, 2011). 0.060 kg of radioactive water has number of moles = .....
2.  $^{35}_{17}\text{Cl}$  and  $^{37}_{17}\text{Cl}$  are two isotopes of chlorine. If atomic mass of chlorine is 35.5, then mass ratio of these isotopes is  $x:1$  where  $x = \dots\dots\dots$
3. Mass of one atom of element is  $6.66 \times 10^{-23}$  g. Number of gram atoms in 0.320 kg of element would be .....
4.  $\text{X}^{2-}$  is isoelectronic of  $_{10}\text{Ne}$ . 1.6 g of  $\text{X}^{2-}$  has 0.1 mole. Thus, there are ..... neutrons in  $\text{X}^{2-}$ .
5. In the following reaction,
- $$\text{SO}_2(\text{g}) + 2\text{H}_2\text{S}(\text{g}) \longrightarrow 3\text{S}(\text{s}) + 2\text{H}_2\text{O}(\text{l})$$
- 2 moles each of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  forms sulphur = ..... moles
6. In the lightest isotope of hydrogen, number of neutrons present is .....
7. Total number of ions in aluminium phosphate is .....
8. 11.2 g of Fe completely react with 3.36 L of  $\text{O}_2$  gas under standard condition to form  $\text{Fe}_x\text{O}_y$ . Thus,  $(x+y)$  is .....

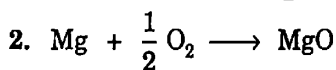
# Answers & Solutions

## Numerical Problem Solving

1. Mass of reactants = mass of products

$$17 + 7.45 = 14.35 + \text{KNO}_3(x)$$

$$\therefore x = 10.10 \text{ g}$$

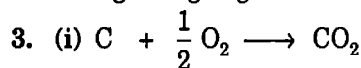


$$24 \text{ g} \quad \left(\frac{32}{2}\right) \text{ g}$$

$$12 \text{ g} \quad 16 \text{ g}$$

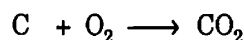
$$? \quad 32 \text{ g}$$

$\text{Mg} = 24 \text{ g}$ .  $\text{MgO}$  has constant composition.



$$12 \text{ g} \quad 16 \text{ g}$$

$$1 \text{ g} \quad \frac{16}{12} \text{ g}$$



$$12 \text{ g} \quad 32 \text{ g}$$

$$1 \text{ g} \quad \frac{32}{12} \text{ g}$$

$$\text{Ratio of oxygen in CO and CO}_2 = \frac{16}{12} : \frac{32}{12} = 1 : 2$$

(ii)

| Carbon | Hydrogen | Amount of hydrogen combines with 12 g carbon | Ratio |
|--------|----------|----------------------------------------------|-------|
| 24 g   | 2 g      | 1 g                                          | 1     |
| 24 g   | 4 g      | 2 g                                          | 2     |
| 24 g   | 6 g      | 3 g                                          | 3     |
| 12 g   | 4 g      | 4 g                                          | 4     |

Ratio of hydrogen in  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$  and  $\text{CH}_4$  that combines with 12 g carbon is  $= 1 : 2 : 3 : 4$ .

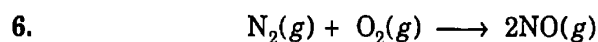
Thus, law of multiple proportion is followed.

4.  $1 : 35.5$

5. (a)  $\text{Mg} = \frac{24}{2} = 12 \text{ g equivalent}^{-1}$

(b)  $\text{Cl}_2 = 35.5 \text{ g equivalent}^{-1}$

(c)  $\text{Ca} = \frac{40}{2} = 20 \text{ g equivalent}^{-1}$



|            |        |        |                                  |
|------------|--------|--------|----------------------------------|
| mass       | 28 g   | 32 g   | $2 \times 30 \text{ g}$          |
| mole       | 1 mol  | 1 mol  | 2 mol                            |
| equivalent | 4      | 4      | 4                                |
|            | 22.4 L | 22.4 L | $2 \times 22.4 \text{ L at NTP}$ |

$$32 \text{ g CO}_2 \equiv 28 \text{ g N}_2$$

$$\therefore 8 \text{ g O}_2 \equiv 7 \text{ g N}_2$$

Thus, equivalent mass of  $\text{N}_2 = 7 \text{ g equivalent}^{-1}$

$$\text{Hence, equivalent of N}_2 \text{ used} = \frac{28}{7} = 4$$

$$\text{Equivalent mass of O}_2 = 8 \text{ g equivalent}^{-1}$$

$$\text{Hence, equivalent used of O}_2 = \frac{32}{8} = 4$$

$$32 \text{ g O}_2 = 2 \times 30 \text{ g NO}$$

$$8 \text{ g O}_2 = 15 \text{ g NO}$$

Thus, equivalent mass of  $\text{NO} = 15 \text{ g equivalent}^{-1}$

Hence, equivalent of  $\text{NO}$  formed  $= 4$

|     | $\text{N}_2$ | $\text{O}_2$ | $\text{NO}$ |
|-----|--------------|--------------|-------------|
| (a) | 7            | 8            | 15          |
| (b) | 1            | 1            | 1           |
| (c) | 1            | 1            | 2           |
| (d) | 1            | 1            | 2           |

7. (i) (a)  $2 \text{ g H}_2 = 26 \text{ g MgH}_2$

$$1 \text{ g H}_2 \equiv 13 \text{ g MgH}_2$$

- (b)  $16 \text{ g O}_2 \equiv 40 \text{ g MgO}$

$$8 \text{ g O}_2 \equiv 20 \text{ g MgO}$$

- (c)  $32 \text{ g O}_2 \equiv 44 \text{ g CO}_2$

$$8 \text{ g O}_2 \equiv 11 \text{ g CO}_2$$

- (d)  $32 \text{ g O}_2 \equiv 46 \text{ g NO}_2$

$$8 \text{ g O}_2 \equiv 11.5 \text{ g NO}_2$$

- (ii) (a) Equivalent of weight  $\text{HCl} = 36.5$

$$\text{hence, equivalents of HCl} = \frac{3.65}{36.5} = 0.1$$

- (b) Equivalent weight of  $\text{H}_2\text{SO}_4 = 49$

$$\text{hence, equivalent of H}_2\text{SO}_4 = \frac{9.8}{49} = 0.2$$

- (c) Equivalent weight of  $\text{H}_3\text{PO}_4 = \frac{98}{3}$

$$\text{hence, equivalents of H}_3\text{PO}_4 = \frac{9.8}{98/3} = 0.3$$

(iii)  ${}^{57}_{27}\text{Co} \mid {}^{58}_{27}\text{Co} \mid {}^{60}_{27}\text{Co} \quad (Z(\text{Co}) = 27)$

# Master Exercises

## Exercise 1

### Short Answer Type Questions

1. Deposition

2. Since, carbonate is =  $60 \text{ g mol}^{-1}$

$$\text{hence, valency} = \frac{\text{molar mass}}{\text{equivalent mass}} = \frac{60}{30} = 2$$

3. Mass of magnesium = 24 g

Mass of oxide = 40 g

Oxygen combined =  $40 - 24 = 16 \text{ g}$

16 g oxygen = 24 g magnesium

$$\therefore 8 \text{ g oxygen} = \frac{24}{16} \times 8 = 12 \text{ g}$$

$\therefore$  Equivalent weight of Mg = 12

4. Mass of aluminium = 27 g

Mass of hydride = 30 g

Hydrogen combined = 3 g

3 g hydrogen = 27 g aluminium

$$\therefore 1 \text{ g hydrogen} = \frac{27}{3} \times 1 = 9 \text{ g}$$

$\therefore$  Equivalent weight of Al = 9

5.  $\text{H}_3\text{PO}_2 + \text{NaOH} \longrightarrow \text{NaH}_2\text{PO}_2$

$\text{H}_3\text{PO}_2 = 1 \text{ NaOH}$

Thus, equivalent weight = molecular weight  
= 66 g equivalent $^{-1}$

6.  $\text{H}_3\text{PO}_3 \longrightarrow \text{NaH}_2\text{PO}_3 \longrightarrow \text{Na}_2\text{HPO}_3$

$\text{H}_3\text{PO}_3 = 1 \text{ H}^+ (\text{NaH}_2\text{PO}_3)$

Equivalent weight = molecular weight  
= 82 g equivalent $^{-1}$

$\text{H}_3\text{PO}_3 = 2 \text{ H}^+ (\text{Na}_2\text{HPO}_3)$

Thus, equivalent weight =  $\frac{\text{molecular weight}}{2}$   
= 41 g equivalent $^{-1}$

Equivalent weight

7.  $\text{H}_3\text{PO}_4 = \text{NaH}_2\text{PO}_4 = 1\text{H}^+$

$$= M = 98$$

$\text{H}_3\text{PO}_4 = \text{Na}_2\text{HPO}_4 = 2\text{H}^+$

$$= \frac{M}{2} = 49$$

$\text{H}_3\text{PO}_4 = \text{Na}_3\text{PO}_4 = 3\text{H}^+$

$$= \frac{M}{3} = 32.66$$

8. Sulphur changes to  $\text{SO}_2$ .

9. (a) 8 (b) 16 (c) 22

10. (a)  $1.6 \text{ g O}_2 = \frac{1.6}{8} = 0.2$  equivalent

$$(b) \frac{0.49}{49} = 0.01 \text{ (equivalent weight of } \text{H}_2\text{SO}_4 = 49)$$

$$(c) \frac{1.80}{9} = 0.2 \text{ (equivalent weight of } \text{H}_2\text{O} = 9)$$

$$(d) \frac{1.6}{4} = 0.4 \text{ (equivalent weight of } \text{CH}_4 = 4)$$

11. (a)  $\text{N}_2 \equiv 6\text{H}$

$$\therefore 1 \text{ H} = \frac{\text{N}_2}{6} = \frac{28}{6} = \frac{M}{6}$$

$2\text{NH}_3 \equiv 6\text{H}$

$$\therefore 1 \text{ H} = \frac{2\text{NH}_3}{6} = \frac{\text{NH}_3}{3} = \frac{17}{3} = \frac{M}{3}$$

(b)  $\text{H}_3\text{PO}_4 \equiv 2\text{OH}^-$

$$\therefore 1 \text{ OH}^- = \frac{\text{H}_3\text{PO}_4}{2} = \frac{M}{2}$$

(c)  $\text{Zn} \equiv 2\text{H}^+$

$$\therefore \text{Equivalent weight of Zn} = \frac{M}{2}$$

(d)  $2\text{FeSO}_4 = 1 (\text{O}) = 16 \text{ g} = 2 \times 8 \text{ g}$

$\therefore 8 \text{ g (O)} = 1 \text{ FeSO}_4$

$\therefore$  Equivalent weight of  $\text{FeSO}_4 = M$

12. Specific heat  $\times$  atomic weight = 6.4

(Dulong and Petit's law)

13. (a) Atomic weight  $\times$  specific heat = 6.4

$$\text{Atomic weight} = \frac{6.4}{0.25} = 25.6$$

$$\therefore \text{Valency} = \frac{\text{atomic weight}}{\text{equivalent weight}} = \frac{25.6}{12.0} = 2.13 \approx 2$$

(b) Thus, (i)  $\text{MCl}_2$  (ii)  $\text{MSO}_4$  (iii)  $\text{M}_2(\text{PO}_4)_2$

$$14. 1.8 \text{ g C}_6\text{H}_{12}\text{O}_6 = \frac{1.8}{180} \text{ mole C}_6\text{H}_{12}\text{O}_6$$

$$= 0.01 \text{ mole}$$

$$= 0.01 \times 6 \text{ moles of carbon}$$

$$= 0.01 \times 6 \times N_0 \text{ atoms of carbon}$$

$$= 0.01 \times 12 \text{ moles of hydrogen}$$

$$= 0.01 \times 12 \times N_0 \text{ atoms of hydrogen}$$

$$= 0.01 \times 6 \text{ moles of oxygen}$$

$$= 0.01 \times 6 \times N_0 \text{ atoms of oxygen}$$

### Analytical Questions

|            | C : H       |
|------------|-------------|
| 1. Benzene | 4.61 : 0.39 |
|            | 12 : 1      |
| Ethane     | 4 : 1       |
| Ethylene   | 6 : 1       |

Thus, mass ratio of C (w.r.t. H = 1 g) in benzene, ethane and ethylene is 6 : 2 : 3

2. For  $\text{NH}_3$ , 0.5014 g H; for  $\text{N}_2\text{H}_4$ , 0.3342 g H.

3.  $\text{N} = 3.6700 \text{ g}$

$\text{H} = 0.5275 \text{ g}$

Total mass of compound  $X = 4.1975 \text{ g}$

$\text{N}(\%) = 87.43\%$

$\text{H}(\%) = 12.57\%$

|   | %     | Ratio |   |
|---|-------|-------|---|
| N | 87.43 | 6.24  | 1 |
| H | 12.57 | 12.57 | 2 |

Thus,  $X$  is  $\text{N}_2\text{H}_4$

$\text{N}$  in  $Y = 10.9578 \text{ g}$ ,  $X$  is  $\text{N}_2\text{H}_4$

4. (a) Neutral species : A, F, G

(b) Negatively charged : B, E

(c) Positively charged : C, D

(d) Conventional symbols

${}^{10}_5\text{A}$ ,  ${}^{14}_7\text{B}^{3-}$ ,  ${}^{39}_{19}\text{C}^+$ ,  ${}^{66}_{30}\text{D}^{2+}$ ,  ${}^{81}_{35}\text{E}^-$ ,  ${}^{11}_5\text{F}$ ,  ${}^{19}_9\text{G}$

5. One carat = 200 mg diamond

24 carat =  $200 \times 24 \times 10^{-3} \text{ g}$

$$= \frac{200 \times 24 \times 10^{-3}}{12} \text{ g atom (mol)}$$

$$= 0.4 \text{ g atom}$$

$$= 0.4 \times 6.02 \times 10^{23} \text{ atom}$$

$$= 2.408 \times 10^{23} \text{ atoms}$$

6. Water = 400 mL = 400 g

$$\therefore \text{D}_2\text{O} = 400 \times \frac{0.015}{100} \text{ g}$$

$$= \frac{400 \times 0.015}{20 \times 100} \text{ moles}$$

$$= 1.8066 \times 10^{21} \text{ molecules}$$

7. 10 millimol  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  in 1000 mL

$$\therefore \text{Millimol per mL} = \frac{10}{1000} = 0.01$$

$$= 0.01 \times 10^{-3} \text{ mol}$$

$$= 1 \times 10^{-5} \text{ mol}$$

$$\text{Mass of } \text{CaCl}_2 \cdot 2\text{H}_2\text{O per mL} = 147 \times 10^{-5} \text{ g mL}^{-1}$$

$$= 1.47 \times 10^{-3} \text{ g mL}^{-1}$$

8. (d)  $\text{NH}_3$

9. Molar of  $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O} = 342 + 18x$

$$\% \text{ of Al} = \frac{54 \times 100}{342 + 18x} = 8.2$$

$$x = 18$$

10. Ca : 38.71 O : 41.29 P : 20.00

11. I

II

|            | %               | Mol  | Ratio |      | %               | Mol  | Ratio |
|------------|-----------------|------|-------|------|-----------------|------|-------|
| Pt =       | 73.3            | 0.38 | 1     | Pt = | 57.9            | 0.30 | 1     |
| Cl =       | 26.7            | 0.75 | 2     | Cl = | 42.1            | 1.18 | 4     |
| Compound : | $\text{PtCl}_2$ |      |       |      | $\text{PtCl}_4$ |      |       |

12.  $x = 6$

13. Let molar mass be =  $M$

If 0.43 g Fe then molar mass = 100 g

$$56 \text{ g Fe then molar mass} = \frac{100 \times 56}{0.43}$$

$$= 13023.26 \text{ g mol}^{-1}$$

14.  $\text{SnF}_2$

15. Cr :  $52 \text{ g mol}^{-1}$

16.  $\text{N}_2\text{O}_4$ ,  $92 \text{ g mol}^{-1}$

## NCERT Problems

1. (i)  $18 \text{ g mol}^{-1}$  (ii)  $44 \text{ g mol}^{-1}$  (iii)  $16 \text{ g mol}^{-1}$

|    | %    | Ratio                       | Integer ratio |
|----|------|-----------------------------|---------------|
| Fe | 69.9 | $\frac{69.9}{55.85} = 1.25$ | 1 = 2         |
| O  | 30.1 | $\frac{30.1}{16.00} = 1.88$ | 1.5 = 3       |

Thus,  $\text{Fe}_2\text{O}_3$

3.  $\text{CuSO}_4 = 159.5 \text{ g mol}^{-1} \equiv 63.5 \text{ g Cu}$

$$\therefore \text{Cu in } 100 \text{ g CuSO}_4 = \frac{63.5}{159.5} \times 100$$

$$= 39.81 \text{ g}$$

4. (i) 6 moles carbon

(ii) 18 moles hydrogen

(iii)  $3 N_0$  molecules ethane

|                 | Atoms                                     |
|-----------------|-------------------------------------------|
| 5. moles in (i) | $\frac{1}{197} \frac{N_0}{197}$           |
| (ii)            | $\frac{1}{23} \frac{N_0}{23}$             |
| (iii)           | $\frac{1}{7} \frac{N_0}{7} \text{ (max)}$ |
| (iv)            | $\frac{1}{71} \frac{N_0}{71}$             |

6.  $6.02 \times 10^{23} \text{ atoms} = 12 \text{ g carbon}$

$$\therefore 1 \text{ atom} = \frac{12}{6.02 \times 10^{23}} \text{ g}$$

7. (i)  $52 N_0$  (ii)  $\frac{52}{N_0} \times N_0 = 52$

$$\text{(iii)} \quad \frac{52}{4} \times N_0$$



## Exercise 2

## Only One Option Correct

1. (a) 2. (b) 3. (c) 4. (b)

5.  $Mg = 0.273 \text{ g}$

Compound of Mg with N = 0.378 g

N-reacted = 0.105 g

|    | Gram  | Mole     | Ratio |   |
|----|-------|----------|-------|---|
| Mg | 0.273 | 0.011375 | 1.51  | 3 |
| N  | 0.105 | 0.0075   | 1     | 2 |

Thus,  $Mg_3N_2$  (a)

$$6. \quad \begin{array}{l} MS_2 = 2S \\ \frac{M + 60}{100} = \frac{64}{40.06} \\ \frac{M + 64}{100} = \frac{64}{40.06} \end{array}$$

$$\therefore M = 96$$

Thus, (d)

7. (c) 8. (c) 9. (a) 10. (b)

11.  $Na_2SO_3 \cdot xH_2O = 126 + 18x$

$$\frac{18x}{126 + 18x} = 0.5$$

$$x = 7$$

Thus, (d)

12. Mass of one atom =  $6.66 \times 10^{-23} \text{ g}$

$$\therefore \text{Atomic mass} = 6.66 \times 10^{-23} \times 6.02 \times 10^{23} \\ = 40 \text{ g mol}^{-1}$$

$$\therefore \text{Number of moles in 40 kg} = \frac{40000 \text{ g}}{40 \text{ g mol}^{-1}} = 1000 \text{ mol}$$

Thus, (a)

13. (c) 14. (d) 15. (c)

$$16. \quad \begin{array}{l} \text{Number of moles of O atoms} = \frac{1}{3} \text{ moles of H} \\ = \frac{3.18 \text{ mol}}{3} = 1.06 \text{ mol} \end{array}$$

Thus, (c)

17. (d)

18. Let molar mass be =  $M$

Mass of 21 carbon atoms = 252

$$\% \text{ of carbon} = \frac{252 \times 100}{M} = 69.98$$

$$\therefore M = 360.1$$

Thus, (d)

19. (a) 20. (b)

$$21. \quad \begin{array}{l} \text{Volume of spherical ball} = \frac{4}{3} \pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (7)^3 \\ \text{Mass} = V \times d = \frac{4}{3} \times \frac{22}{7} \times (7)^3 \times 1.4 \text{ g} \end{array}$$

$$Fe (56\%) = \frac{4}{3} \times \frac{22}{7} \times (7)^3 \times 1.4 \times \frac{56}{100} \text{ g} = 1126.4$$

$$\text{Moles} = 20$$

Thus, (c)

22. (a) 23. (a) 24. (b) 25. (b)

## One or More Than One Options Correct

1. (a, b, c) 2. (a, c) 3. (a, b, c)  
 4. (a, c, d) 5. (a, b, d) 6. (a, c)  
 7. (a, b, c) 8. (d) 9. (a, b) 10. (a, b, d)

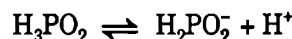
## Brain Twisters



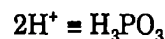
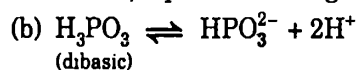
$$1 H^+ \equiv 1 H_3O^+$$

$$\therefore \text{Equivalent weight of } H_3O^+ = \text{molecular weight} \\ = 19 \text{ g equivalent}^{-1}$$

2. Equivalent weight in acid is based on number of ionisable protons which is called Basicity. **Ionisable hydrogen is attached to electronegative atom as O, and X (X = F, Cl, Br, I)**

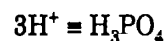
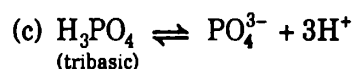
(a)  $H_3PO_2$  has one ionisable hydrogen (monobasic acid)

hence, equivalent weight = molecular weight



$$\therefore 1 H^+ \equiv \frac{H_3PO_3}{2}$$

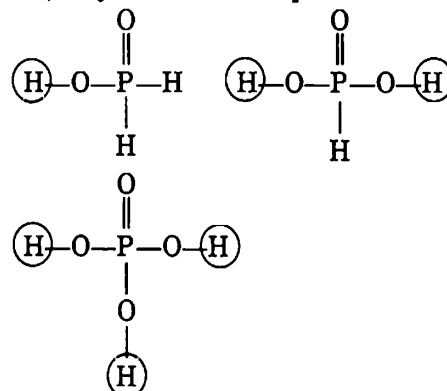
$$\text{Hence, equivalent weight} = \frac{\text{molecular weight}}{2}$$



$$1 H^+ \equiv \frac{H_3PO_4}{3}$$

$$\text{hence, equivalent weight} = \frac{\text{molecular weight}}{3}$$

(In the Unit-Chemical Bonding, structures have been given; they can be used to predict ionisable hydrogens).



Ionisable hydrogens (circled) are attached to oxygen atoms.

3. (a)  $32 \text{ g O}_2 \equiv 12 \text{ g C}$

$8 \text{ g O}_2 \equiv 3 \text{ g C}$

(b)  $4 \text{ g H}_2 \equiv 12 \text{ g C}$

$1 \text{ g H} \equiv 3 \text{ g C}$

(c)  $2 \text{ g H}_2 \equiv 24 \text{ g C}$

$1 \text{ g H}_2 \equiv 12 \text{ g C}$

(d)  $4 \text{ g H}_2 \equiv 24 \text{ g C}$

$1 \text{ g H}_2 \equiv 6 \text{ g C}$

(e)  $6 \text{ g H}_2 \equiv 24 \text{ g C}$

$1 \text{ g H}_2 \equiv 4 \text{ g C}$

(f)  $8 \text{ g H}_2 \equiv 36 \text{ g C}$

$1 \text{ g H}_2 \equiv 4.5 \text{ g C}$

Equivalent weight is not a definite property. It depends on the reaction and product formed.

#### 4. Molecular weight

Let A be  $\text{S}_x\text{O}_y$   $32x + 16y$

and B be  $\text{S}_p\text{O}_q$   $32p + 16q$

In A  $16y \text{ g oxygen} \equiv (32x + 16y) \text{ g S}_x\text{O}_y$

hence,  $8 \text{ g oxygen} \equiv \frac{32x + 16y}{2y} = 16 \text{ (given)}$

$$\frac{32x}{y} + 8 = 16$$

$$\frac{x}{y} = \frac{1}{2} = \frac{\text{number of S atom}}{\text{number of O atom}}$$

Thus, A is  $\text{SO}_2$

In B  $16q \text{ g oxygen} \equiv (32p + 16q) \text{ g S}_p\text{O}_q$

$8 \text{ g oxygen} \equiv \frac{32p + 16q}{2q} = 13.33 \text{ (given)}$

$$\frac{16p}{q} = 5.33$$

$$\frac{p}{q} = \frac{5.33}{16} = \frac{1}{3} = \frac{\text{number of S-atom}}{\text{number of O-atom}}$$

Thus, B is  $\text{SO}_3$

#### 5. Hydrides

(I)  $\text{N}_x\text{H}_y$

molar mass  $= (14x + y)$

$y \text{ g H} = (14x + y) \text{ g N}_x\text{H}_y$

$1 \text{ g H} \equiv \frac{14x + y}{y} = 5.66$

$$\frac{14x}{y} = 4.66$$

$$\frac{x}{y} = \frac{1}{3} = \frac{\text{number of nitrogen atom}}{\text{number of hydrogen atom}}$$

Hence, hydrogen is  $\text{NH}_3$

(II)  $\frac{14x + y}{y} = 8 \text{ (given)}$

$$\frac{14x}{y} = 7$$

$$\frac{x}{y} = \frac{1}{2} = \frac{\text{number of nitrogen atom}}{\text{number of hydrogen atom}}$$

Thus, hydride appears  $\text{NH}_2$  (unstable).

Thus, actual hydride is  $\text{N}_2\text{H}_4$  (hydrazine).

6. (a)  $200 \text{ g parts per million (out of } 10^6 \text{ g)}$

$$= \frac{200}{1000} \text{ moles CaCO}_3 \text{ per million gram}$$

$$= 2000 \text{ millimoles CaCO}_3 \text{ per million gram}$$

$$= \frac{2000}{10^6} = 2 \times 10^{-3} \text{ millimoles per gram}$$

(b)  $2 \text{ moles CaCO}_3$

$$= 2 \times N_0 \text{ molecules CaCO}_3 \text{ per million gram}$$

$$= \frac{2 \times N_0}{10^5} \text{ molecules per gram}$$

7. Purity  $= \frac{20}{24} \times 100 = \frac{250}{3} \text{ g}$

(24 carat is assumed to be 100%)

Pure diamond in 200 mg sample

$$= \frac{200}{1000} \times \frac{250}{3} \times \frac{1}{100} = \frac{1}{6} \text{ g}$$

Number of moles  $= \frac{1}{6} \times \frac{1}{12} \text{ g carbon}$

Number of carbon atoms

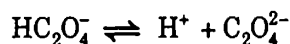
$$= \frac{6.02 \times 10^{23}}{72} = 8.33 \times 10^{21} \text{ atom}$$

8. 1 mole ethyl alcohol = 46 g ethyl alcohol ( $\text{CH}_3\text{CH}_2\text{OH}$ )

Water present  $= 100 - 46 = 54 \text{ g}$

Moles of  $\text{CH}_3\text{CH}_2\text{OH} = \frac{46}{46} = 1$

Moles of  $\text{H}_2\text{O} = \frac{54}{18} = 3$ , Ratio = 1 : 3



One of the students (say A) would have derived equivalent weight based on  $\text{H}^+$  which is = molecular weight

Another student (say B) would have derived equivalent weight based on  $\text{C}_2\text{O}_4^{2-}$  (oxalate)

10. Magnesium = 0.24 g

Magnesium oxide (residue) = 0.40 g

Oxygen combined = 0.16 g

0.16 g oxygen  $\equiv 0.24 \text{ g Mg}$

Thus, 8 g oxygen = 12 g Mg

11. (a)  $\text{NH}_4\text{NO}_3 = \frac{28 \times 100}{80}$

(b)  $\text{NH}_2\text{CONH}_2 = \frac{28 \times 100}{60} \text{ Max}$

(c)  $\text{KNO}_3 = \frac{14}{101} \times 100 \text{ least}$

(d)  $\text{NH}_4\text{Cl} = \frac{14 \times 100}{53.5}$



Based on valency, equivalent weight of

$$\text{Ca}_3(\text{PO}_4)_2 = \frac{\text{molecular weight}}{6}$$

Hence, one equivalent  $\text{Ca}_3(\text{PO}_4)_2 = \frac{\text{mole}}{6}$

$$1 \text{ mole } \text{Ca}_3(\text{PO}_4)_2 = 3 \text{ moles } \text{CaCl}_2 = 2 \text{ moles } \text{H}_3\text{PO}_4$$

$$\therefore \frac{1}{6} \text{ mole } \text{Ca}_3(\text{PO}_4)_2 = \frac{1}{2} \text{ mole } \text{CaCl}_2 = \frac{1}{3} \text{ mole } \text{H}_3\text{PO}_4$$

## Passage Comprehension Questions

### Passage 1

1. (a) Dish of 20 cm diameter (10 cm = 0.1 m radius)  
has area =  $\pi r^2 = \pi \times 0.01 \text{ m}^2$   
 $0.21 \times 10^{-18} \text{ m}^2$  is the area of = 1 molecule  
 $\therefore \pi \times 0.01 \text{ m}^2$  is the area of =  $\frac{\pi \times 0.01}{0.21 \times 10^{-18}}$  molecules

$$1.4 \times 10^{-4} \text{ g stearic acid} = \frac{1.4 \times 10^{-4}}{284} \text{ mol}$$

$$= \frac{1.4 \times 10^{-4}}{284} N_0 \text{ molecules}$$

$$\frac{1.4 \times 10^{-4} N_0}{284} = \frac{\pi \times 0.01}{0.21 \times 10^{-18}}$$

$$N_0 = 3.03 \times 10^{23}$$

2. (b)  $\frac{1}{N_0} = \frac{1}{3.03 \times 10^{23}} = 3.33 \times 10^{-24} \text{ g}$

### Passage 2

1. (b) Rs. 50 per kg = Rs. 50 per  $\left(\frac{1000}{74.5}\right) \text{ mol}$

$$\text{cost} = \frac{\text{Rs. 50}}{\frac{1000}{74.5}} \text{ per mol} = \text{Rs. 3.73 per mol}$$

2. (c)  $1 \text{ kg KCl} = \frac{1000}{74.5} \text{ mol K}^+$  costing Rs. 50/-

$$\text{Re 1 gives} = \frac{1000}{74.5 \times 50} \text{ mol of K}^+ \text{ (in KCl)}$$

$$1 \text{ kg K}_2\text{SO}_4 = \frac{1000}{174} \text{ mol}$$

$$= \frac{2000}{174} \text{ mol K}^+ \text{ costing Rs. } x$$

$$\text{Re 1 gives} = \frac{1000 \times 2}{174x} \text{ mol of K}^+ \text{ (in K}_2\text{SO}_4\text{)}$$

$$\therefore \frac{1000}{74.5 \times 50} = \frac{2000}{174x}$$

$$x = \text{Rs. 42.82 kg}^{-1}$$

3. (d) Let mass of  $\text{K}_2\text{O} = x \text{ g}$

$$= \frac{x}{94} \text{ mol K}_2\text{O} = \frac{2x}{94} \text{ mol K}^+$$

$$1000 \text{ g KCl} = \frac{1000}{74.5} \text{ mol KCl} = \frac{1000}{74.5} \text{ mol K}^+$$

$$\therefore \frac{2x}{94} = \frac{1000}{74.5}$$

$$x = 631 \text{ g} = 0.631 \text{ kg}$$

### Passage 3

1. (a) 2. (c)  
3. (b) For spectrum, approximate percentage of

$$^{24}\text{Mg} = 80$$

$$^{25}\text{Mg} = 8$$

$$^{26}\text{Mg} = 12$$

$$\text{Average atomic mass} = \frac{M_1X_1 + M_2X_2 + M_3X_3}{100} = 24.32$$

## Assertion & Reason

1. (a) 2. (b) 3. (d) 4. (a)

## True & False

1. F(16) 2. T 3. T 4. T 5. F (moles one equal)  
6. F (no  $\text{H}_2$  is left) 7. T 8. T 9. T  
10. F (it is  $\frac{17}{3} \text{ g}$ )

## Fill in the Blanks

1. multiple proportion 2. 2:3 3.  $\text{C}_2\text{H}_6$  4. 20  
5. 0.33 6.  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$  7.  $10^3$  8. 1  
9. reciprocal proportions 10. Dalton (Da)

## Matrix-Match Type Questions

### I. Only One Correct

1. (A) — (4); (B) — (3); (C) — (1);  
(D) — (2); (E) — (5)  
2. (A) — (5); (B) — (3); (C) — (1);  
(D) — (4); (E) — (2)

### II. One or More Correct

1. (A) — (1,3,4,5); (B) — (1,2,3,5); (C) — (1,3,5);  
(D) — (1,3,5)  
2. (A) — (1,2,3,4,5); (B) — (1,3,5); (C) — (1);  
(D) — (4)

## Integer Answer Types

### Set I

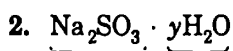
|             |   |   |   |   |   |   |   |   |
|-------------|---|---|---|---|---|---|---|---|
| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Answers →   | 3 | 7 | 1 | 0 | 1 | 0 | 6 | 5 |
|             | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
|             | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|             | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
|             | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
|             | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
|             | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
|             | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
|             | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
|             | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
|             | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |

1.  $\text{CH}_4 = 16 \text{ g mol}^{-1}$

4g H has = 12 g carbon

Thus, 1 g H has =  $\frac{12}{4} = 3 \text{ g}$

Thus,  $x = 3$



126 g    18 y

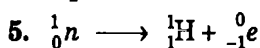
$$\frac{18y}{126 + 18y} = \frac{50}{100}$$

$y = 7$

3. 1 amu

4.  $\text{H}_2^{2+}$  has = 2 electron, 0 neutron

$\text{H}_2^{2+}$  has = 0 electron, 0 neutron



due to emission of electron, atomic number increases by 1 unit

6.  $\text{Na}_2\text{CO}_3$  is thermally stable, no effect of heating.

7. Empirical formula weight = 30

Thus,  $\frac{180}{30} = 6$

8.  $\frac{2.495}{249.5} = 0.01 \text{ mol}$

= 0.01x  $\text{H}_2\text{O}$

= 0.05 mol

$\therefore x = 5$

## Set II

|             |   |   |   |   |   |   |   |   |
|-------------|---|---|---|---|---|---|---|---|
| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Answers →   | 3 | 3 | 8 | 8 | 3 | 0 | 2 | 5 |
|             | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
|             | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|             | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
|             | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
|             | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
|             | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
|             | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
|             | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
|             | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
|             | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |

1. Radioactive water is heavy water with heavy isotope ( ${}^2_1\text{H}$ ) of hydrogen. Thus, molar mass of heavy water =  $2 \times 2 + 16$

= 20 g mol<sup>-1</sup>

0.060 kg = 0.060 × 1000 g = 60 g =  $\frac{60}{20} = 3 \text{ moles}$

Thus, 3

2. Average atomic mass =  $\frac{A_1X_1 + A_2X_2}{x_1 + x_2}$

$$= \frac{35x + 37}{x + 1} = 35.5$$

Thus,  $x = 3$

3. One gram atom has  $N_0$  atoms =  $6.02 \times 10^{23}$  atoms

If atomic mass = A

then mass of one atom =  $\frac{A}{N_0} = 6.66 \times 10^{-23} \text{ g}$

$\frac{A}{N_0} = 6.66 \times 10^{-23}$

$\therefore A = 6.66 \times 10^{-23} \times 6.02 \times 10^{23}$

$$= 40 \text{ g mol}^{-1}$$

Number of gram atoms (moles) in 0.320 kg

=  $\frac{0.320 \times 1000}{40} = 8$

4.  $X^{2-}$  is isoelectronic with Ne.

Thus, electrons in  $X^{2-} = 10$

Proton (= atomic number) in  $X^{2-} = 8$

Also mole =  $\frac{\text{Mass}}{\text{atomic mass}}$

$0.1 = \frac{1.6}{A}$

$\therefore A = 16$

Also, neutrons + protons = Atomic mass = 16

$\therefore$  neutrons = 16 - 8 = 8

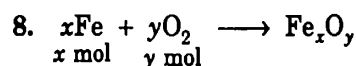
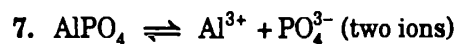


As per equation 1 mol    2 mol    3 mol    2 mol  
taken :    2 mol    2 mol    ?

If one takes 2 moles  $\text{SO}_2(g)$  then 4 moles of  $\text{H}_2\text{S}(g)$  are required. But 2 moles of  $\text{H}_2\text{S}(g)$  have been taken. Hence,  $\text{H}_2\text{S}(g)$  is **limiting reagent** that forms 3 moles of sulphur.

Thus, 3

6.  ${}_1^1\text{H}$  neutrons = 0



= (22.4 y L)     $\frac{x}{0.2} = \frac{22.4y}{3.36}$

$11.2 \text{ g} = \frac{11.2}{56} = 0.2 \text{ mol}$

$\frac{x}{0.2} = \frac{22.4y}{3.36}$

$\frac{x}{y} = \frac{2}{3}$

Thus,  $\text{Fe}_2\text{O}_3$   $x + y = 5$



# Chemical Bonding

The theory of the chemical bond ..... is still far from perfect. Most of the principles that have been developed are crude, and only rarely can they be used in making an accurate quantitative prediction. However, they are the best that we have, as yet, and I agree with Poincare's that "it is far better to forsee even without certainty than not to forsee at all".

Linus Pauling

## Quick Points

- Formal charge is given by

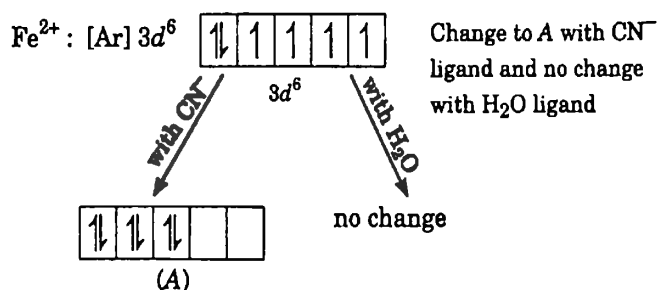
$$F = v - \frac{s}{2} - u$$

where  $v$  = valence electron

$s$  = shared electrons forming bonds

$u$  = unshared electrons

- $1 \text{ pm} = 1 \times 10^{-12} \text{ m} = 1 \times 10^{-10} \text{ cm}$
- Charge on electron =  $4.8 \times 10^{-10} \text{ esu}$   
 $= 1.6 \times 10^{-19} \text{ C}$
- In a complex,  $[ML_n]$ ,  $M$  is the metal and  $L$  the ligand and  $n$  the number of ligands.
- If ligand is weak, (as  $\text{H}_2\text{O}$ ) arrangement of electrons in valence shell is not affected but with strong ligand, (as  $\text{CN}^-$ ) unpaired electrons get paired.



- If there are  $N$  unpaired electrons, magnetic moment is given by

$$\mu = \sqrt{N(N+2)} \text{ BM}$$

## Learning Framework of the Chapter

- Ionic Bonding
- Covalent Bonding
- Coordinate Bonding
- Formal charge
- VSEPR Theory
- Assessing Molecular Shape
- Sigma and Pi Bonds
- Valence Bond Theory
- Hybridisation
- Molecular Orbital Theory
- Bonding in Complexes
- Dipole Moment
- Fajan's Rule
- Hydrogen Bonding
- Resonance
- Metallic Bonding

A molecule will only be formed, if it is more stable, and has a lower energy than the individual atoms. Normally only electrons in the outermost shell of an atom are involved in forming bonds and in this process each atom attains a stable electronic configuration of inert gas. We divide elements into three classes :

- (A) Electropositive elements, whose atoms give up one or more electrons easily. They have low ionisation potentials.
- (B) Electronegative elements, which can gain electrons. They have higher value of electronegativity.
- (C) Elements which have little tendency to lose or gain electrons.

## Types of Bonds

|       | Atoms Involved                                                                                 | Bonding    |
|-------|------------------------------------------------------------------------------------------------|------------|
| (i)   | A + B                                                                                          | Ionic      |
| (ii)  | B + B                                                                                          | Covalent   |
| (iii) | A + A                                                                                          | Metallic   |
| (iv)  | Electron deficient molecule or ion (Lewis acid) and electron-rich molecule or ion (Lewis base) | Coordinate |
| (v)   | H and electronegative element (N, O, F)                                                        | Hydrogen   |

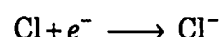
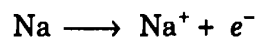
Table 2.1 Simple Binary Ionic Compounds

| Group    |   |           |   | General formula | Ions present         | Example                        | Melting point (°C) |
|----------|---|-----------|---|-----------------|----------------------|--------------------------------|--------------------|
| Metal    |   | Non-metal |   |                 |                      |                                |                    |
| IA(1)    | + | VIIA(17)  | → | $MX$            | $(M^+, X^-)$         | LiBr                           | 547                |
| IIA(2)   | + | VIIA(17)  | → | $MX_2$          | $(M^{2+}, 2X^-)$     | MgCl <sub>2</sub>              | 708                |
| IIIA(13) | + | VIIA(17)  | → | $MX_3$          | $(M^{3+}, 3X^-)$     | GaF <sub>3</sub>               | 800 (subl)         |
| IA(1)    | + | VIA(16)   | → | $M_2X$          | $(2M^+, X^{2-})$     | Li <sub>2</sub> O              | > 1700             |
| IIA(2)   | + | VIA(16)   | → | $MX$            | $(M^{2+}, X^{2-})$   | CaO                            | 2580               |
| IIIA(13) | + | VIA(16)   | → | $M_2X_3$        | $(2M^{3+}, 3X^{2-})$ | Al <sub>2</sub> O <sub>3</sub> | 2045               |
| IA(1)    | + | VA(15)    | → | $M_3X$          | $(3M^+, X^{3-})$     | Li <sub>3</sub> N              | 840                |
| IIA(2)   | + | VA(15)    | → | $M_3X_2$        | $(3M^{2+}, 2X^{3-})$ | Ca <sub>3</sub> P <sub>2</sub> | ~1600              |
| IIIA(13) | + | VA(15)    | → | $MX$            | $(M^{3+}, X^{3-})$   | AlP                            |                    |

- Cations and anions attain stable noble gas configuration with outer shell octet of electrons. In some cases cations may not have octet but different outer-shell (see Tables 2.2 and 2.3)
- In the solid state each cation surrounds itself with anions, and each anion with cations. These very large number of ions are arranged in an orderly network called **ionic crystal**.
- Ionic solids
  - are good conductor of electricity in fused state and in aqueous solution,

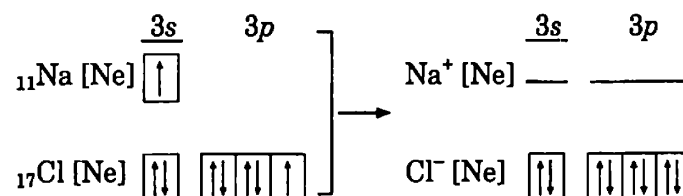
## Ionic Bonding

- An ionic bond is formed when a **metal atom** transfers one or more electrons to a **non-metal atom**.



As a result of this transfer the metal atom becomes **cation** and the non-metal the **anion**. IA(1), IIA(2) and VIA(16), VIIA(17) elements are involved (Table 2.1).

- We can understand this exchange of electrons by showing electron configuration.



- are soluble in polar solvents and insoluble in non-polar solvents,
- have high m.p. and b.p.,
- have strong force of attraction between cation and anion (Coulombic force)

$$F = \frac{z_1 z_2 e^2}{Dr^2}$$

where  $z_1$  and  $z_2$  are charges on the ions,  $e$  the electronic charge;  $D$  the dielectric constant of the medium and  $r$  the inter-ionic distance (i.e., the bond length).

Table 2.2 Electronic Configuration of Some Metal Ions

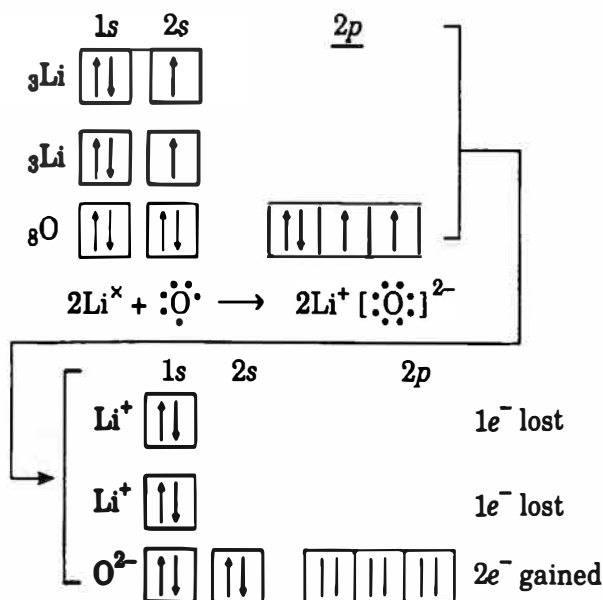
| "Octet".                           | "18"                             | "18 + 2"         | Variable                              |
|------------------------------------|----------------------------------|------------------|---------------------------------------|
| Na <sup>+</sup> , Mg <sup>2+</sup> | Cu <sup>+</sup> Zn <sup>2+</sup> | In <sup>+</sup>  | Cr <sup>2+</sup> [Ar] 3d <sup>4</sup> |
| K <sup>+</sup> , Ca <sup>2+</sup>  | Ag <sup>+</sup> Cd <sup>2+</sup> | Tl <sup>+</sup>  | Cr <sup>3+</sup> [Ar] 3d <sup>3</sup> |
| Rb <sup>+</sup> , Sr <sup>2+</sup> | Au <sup>+</sup> Hg <sup>2+</sup> | Sn <sup>2+</sup> | Mn <sup>2+</sup> [Ar] 3d <sup>5</sup> |
| Cs <sup>+</sup> , Ba <sup>2+</sup> | Ga <sup>3+</sup>                 | Pb <sup>2+</sup> | Mn <sup>3+</sup> [Ar] 3d <sup>4</sup> |
| Fr <sup>+</sup> , Ra <sup>2+</sup> | Sb <sup>3+</sup>                 | Sb <sup>3+</sup> | Fe <sup>2+</sup> [Ar] 3d <sup>6</sup> |
| Al <sup>3+</sup>                   | Tl <sup>3+</sup>                 | Bi <sup>3+</sup> | Fe <sup>3+</sup> [Ar] 3d <sup>5</sup> |
| Sc <sup>3+</sup>                   |                                  |                  | Co <sup>2+</sup> [Ar] 3d <sup>7</sup> |
| Y <sup>3+</sup>                    |                                  |                  | Co <sup>3+</sup> [Ar] 3d <sup>6</sup> |
| La <sup>3+</sup>                   |                                  |                  | Ni <sup>2+</sup> [Ar] 3d <sup>8</sup> |
|                                    |                                  |                  | Ni <sup>3+</sup> [Ar] 3d <sup>7</sup> |

Table 2.3 Lewis Dot Formulae for Representative Elements

| Group                                | IA<br>(1) | IIA<br>(2) | IIIA<br>(13) | IVA<br>(14)  | VA<br>(15)   | VIA<br>(16)  | VIIA<br>(17) | 0<br>(except He) |
|--------------------------------------|-----------|------------|--------------|--------------|--------------|--------------|--------------|------------------|
| Number of electrons in valence shell | 1         | 2          | 3            | 4            | 5            | 6            | 7            | 8                |
| Period 1                             | H •       |            |              |              |              |              |              | He:              |
| Period 2                             | Li •      | Be: ••     | B • • • • •  | C • • • • •  | N • • • • •  | O • • • • •  | F • • • • •  | Ne:              |
| Period 3                             | Na •      | Mg: ••     | Al • • • • • | Si • • • • • | P • • • • •  | S • • • • •  | Cl • • • • • | Ar:              |
| Period 4                             | K •       | Ca: ••     | Ga • • • • • | Ge • • • • • | As • • • • • | Se • • • • • | Br • • • • • | Kr:              |
| Period 5                             | Rb •      | Sr: ••     | In • • • • • | Sn • • • • • | Sb • • • • • | Te • • • • • | I • • • • •  | Xe:              |
| Period 6                             | Cs •      | Ba: ••     | Tl • • • • • | Pb • • • • • | Bi • • • • • | Po • • • • • | At • • • • • | Rn:              |
| Period 7                             | Fr •      | Ra:        |              |              |              |              |              |                  |

**Illustration 1** Explain the formation of Li<sub>2</sub>O based on electrons configuration.

**Solution** The Lewis dot formula for the atoms and ions are



## Solubility of Ionic Solids

By the Coulombic force of attraction ( $F$ ) between cation and anion.

$$F = \frac{z_1 z_2 e^2}{Dr^2}$$

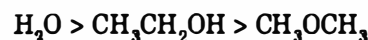
we can study the solubility of ionic solids in different solvents.

### DEEP Focus

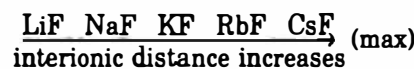
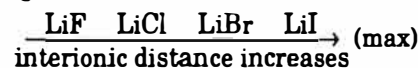
- Greater the force of attraction between ions, smaller the tendency of the ions to go into solution and thus, smaller the solubility.
  - For a given solute, greater the value of  $D$  (Dielectric constant of the solvent) then smaller the force of attraction between positive and negative ions, hence greater the solubility.

$$D(\text{H}_2\text{O}) > D(\text{CH}_3\text{CH}_2\text{OH}) > D(\text{CH}_3\text{OCH}_3)$$

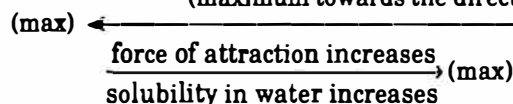
hence solubility of ionic solid (say NaCl) in



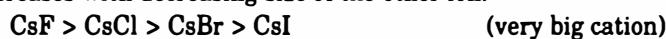
- Greater the interionic distance ( $r$ ) between positive and negative ions, smaller the force of attraction between positive and negative ions hence greater the solubility in the given solvent



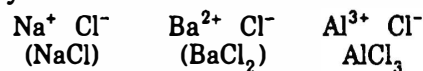
(maximum towards the direction of arrow)



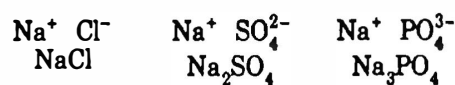
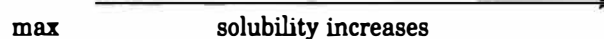
However, if one of the ions is very big, the solubility increases with decreasing size of the other ion.



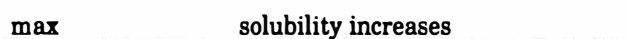
- Also, greater the charge ( $z_1$  and  $z_2$ ) then greater the force of attraction between positive and negative ions hence smaller the tendency of the ions to go into the solution hence smaller the solubility.



charge increases max



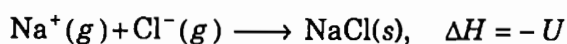
charge increases max



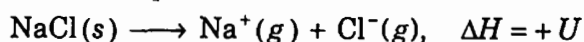
## Energetics of Ionic Bond Formation

The energy given off when gaseous positive and negative ions come together to form 1 mole of the solid ionic compound is called **lattice energy** ( $U$ ).



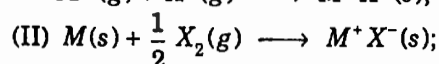
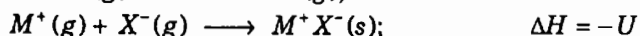
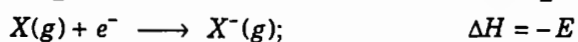
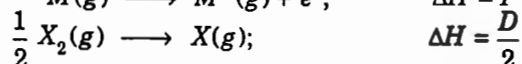
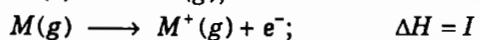
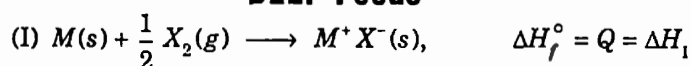


For the reverse process



Lattice energy can be calculated using **Born-Haber cycle**

### DEEP Focus



$$\Delta H_2 = S + I + \frac{D}{2} - E - U$$

where  $\Delta H_f^\circ$  is the standard heat of formation of  $MX(s)$ ,

$S$  = the heat of sublimation of  $M(s)$ ,

$I$  = the ionisation energy of  $M(g)$

$D$  = the dissociation energy of  $X_2(g)$ ,

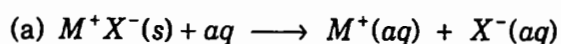
$E$  = the electron-affinity of  $X(g)$

$I$  and  $II$  represent the same chemical change hence,

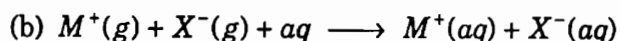
$$\Delta H_1 = \Delta H_2$$

$$\therefore Q = S + I + \frac{D}{2} - E - U$$

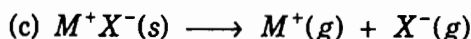
$$\therefore U = S + I + \frac{D}{2} - E - Q$$



$$\text{enthalpy change} = \Delta H_{\text{soln}}$$



$$\text{enthalpy change} = \Delta H_{\text{Hydration}}$$



$$\text{enthalpy change} = U$$

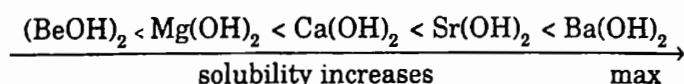
We find  $(a) = (b) + (c)$

$$\therefore \Delta H_{\text{soln}} = \Delta H_{\text{Hydration}} + U$$

Both lattice energy and hydration energies decrease with increase in ionic size.

### DEEP Focus

- If the anion and the cation are of comparable size, the cationic radius will influence the lattice energy. Since lattice energy decreases much more than the hydration energy with increasing ionic size, solubility will increase as we go down the group.



- If the anion is large compared to the cation, the lattice energy will remain almost constant within a particular group. Since the hydration energies decrease down a group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.

## Covalent Bonding

If duplet (2) or octet (8) is completed by sharing of electrons between two electronegative elements, the bond formed is called **covalent bond**.

## The Lewis Theory

### The Octet rule

For many light atoms a stable arrangement is attained when the atom is surrounded by eight electrons—the octet rule. (In case of  $H_2$ , duplet is completed)

- Number of bonds between two atoms

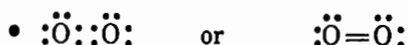
$$= \frac{\text{electrons shared}}{2}$$

| Molecule                                                                                    | Electrons shared    | Bonds                  |                                                              |
|---------------------------------------------------------------------------------------------|---------------------|------------------------|--------------------------------------------------------------|
| $H : H$                                                                                     | 2                   | 1 (single)             | $H - H$                                                      |
| $:\ddot{O} : \ddot{O} :$                                                                    | 4                   | 2 (double)             | $O = O$                                                      |
| $:\text{N} :: \text{N} :$                                                                   | 6                   | 3 (triple)             | $N \equiv N$                                                 |
| $:\ddot{O} : \text{H}$<br>$\text{H}$                                                        | 2 (between H and O) | 1 (two single bonds)   | $\begin{array}{c} O - H \\   \\ H \end{array}$               |
| $\text{H} : \text{N} : \text{H}$<br>$\text{H}$                                              | 2 (between H and N) | 1 (three single bonds) | $\begin{array}{c} H - N - H \\   \\ H \end{array}$           |
| $\begin{array}{c} H \\ \times \\ \text{H} : \text{C} : \text{H} \\ \times \\ H \end{array}$ | 2 (between H and C) | 1 (four single bonds)  | $\begin{array}{c} H \\   \\ H - C - H \\   \\ H \end{array}$ |

- All the valence (outer-shell) electrons of the atoms in a Lewis structure must be shown in the structure.
- Usually, all the electrons in a Lewis structure are paired.

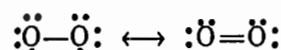


### DEEP Focus



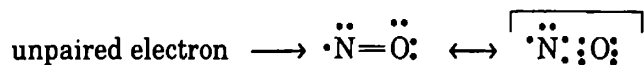
This is actually incorrect since it does not have unpaired electrons which account for the paramagnetic character of  $O_2$  (by MO theory,  $O_2$  is said to have two unpaired electrons.)

A resonance hybrid of the following two contributing structures has unpaired electrons and also conforms to the fact that the experimentally measured bond length in  $O_2$  shows to have some multiple bond character.



- If there are odd number of electrons (15 as in NO), then there is at least one unpaired electron somewhere in the structure.
- At least one atom lacks a completed octet of electrons and species is paramagnetic.

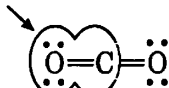
complete octet of N and O



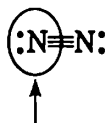
electrons shared between N and O = 5

number of bonds = 2.5

Octet of electrons around each oxygen atom (four in double bonds and four in lone pairs)



Octet of electrons around carbon atom (four in each of two double bonds)



Octet of electrons around each N atom (Six in triple bond and two in lone pair)

- A mathematical relationship can be used to determine total number of electrons shared :

$$S = N - A$$

where  $S$  is the total number of electrons shared in the molecule or polyatomic ion;  $N$  is the number of valence shell electrons needed by all the atoms in the molecule or ion to achieve noble gas configurations ( $N = 8 \times \text{number of atoms (H excluded)} + 2 \times \text{number of H atoms}$ );  $A$  is the number of electrons available in the valence shell of all of the representative atoms. This is equal to the sum of their periodic group numbers.

In  $\text{CO}_2$ ,  $A$  for each O atom is 6 and for C atom is 4.

Thus,  $A = 4 + 2 \times 6 = 16$

$$N = 8 \times 3 = 24$$

Thus,  $S = 24 - 16 = 8$ .

Thus, there are, eight electrons shared to form bonds

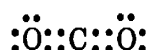


**Illustration 1** Calculate total number of shared electrons in  $\text{H}_2\text{SO}_4$  and thus, assign structure.

**Solution** Let  $S$  be the total number of shared electrons then

$$S = N - A$$

where  $N$  is the number of valence shell electrons needed by all atoms in a molecule or ion and  $A$  is the number of electrons available in the valence shell of all of the representative atoms

$$N = 8 \times \text{number of atoms (excluding H)} + 2 \times \text{number of H-atoms}$$

$$A = \text{sum of the periodic group number of atoms.}$$

In  $\text{H}_2\text{SO}_4$ .

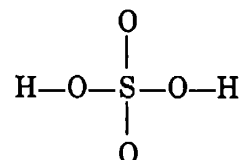
$$N = 8 \times 5 \text{ (one sulphur and four oxygen)} + 2 \times 2 \text{ (H)} = 44$$

$$A = 2 \text{ (for two H-atoms)} + 6 \text{ (for sulphur atom)} + 24 \text{ (for four oxygen atoms)}$$

$$= 32$$

$$\therefore S = 44 - 32 = 12$$

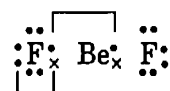
Thus,  $\text{H}_2\text{SO}_4$  has six  $\sigma$ -bonds (each bond is formed by sharing of one pair of electrons)



## Exceptions to the Octet Rule

In so many cases, the octet rule is violated :

- In  $\text{BeF}_2$ , octet of Be is not complete  
octet incomplete



octet complete

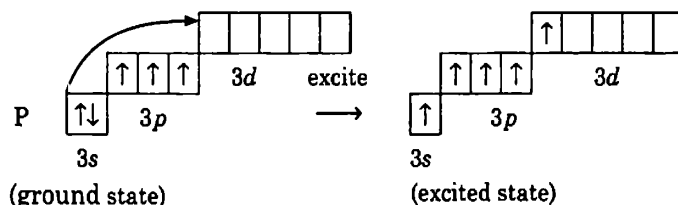
- In  $\text{BF}_3$ , octet of B is not complete



octet incomplete [ $\text{B} \times \text{F} \cdot$ ] octet complete



- The octet rule is also violated where atoms have an extra energy level which is close in energy to the  $p$  level, and may accept electrons and be used for bonding.  $\text{PF}_3$  obeys the octet rule, but  $\text{PF}_5$  does not.  $\text{PF}_5$  has ten outer electrons, and uses one  $3s$ , three  $3p$  and one  $3d$  orbitals



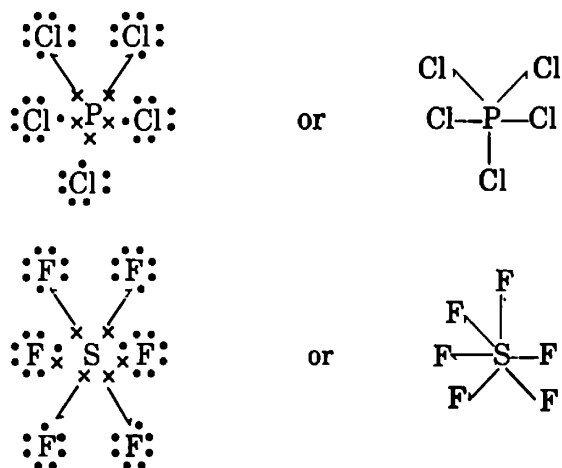
Any compound with more than four covalent bonds must violate the octet rule, and these become very common in the elements after the first two periods of eight elements in the Periodic Table.

In  $\text{SF}_6$ , there are six S—F bonds having in all 12 electrons in sulphur.



In  $\text{PCl}_5$ , there are ten electrons in phosphorus. In such cases, **Sugden** introduced **singlet linkage** in which one electron is donated (instead of one pair of electrons) to the

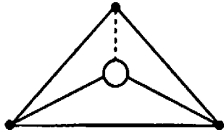
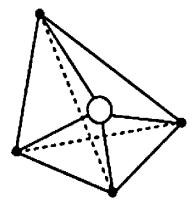
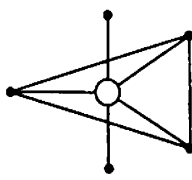
electron deficient atom so that octet rule is not violated. This is indicated by (—). Thus,  $\text{PCl}_5$  and  $\text{SF}_6$  are represented as



## Sidgwick-Powell Theory

Depending on the number of electron pairs in the outer-shell of the central atom, shape of the molecule can be decided based on this theory. In this concept bond pairs and lone pairs are taken as equivalent since all electron pairs take up some space, and also their tendency of repulsion. This repulsion is minimised if the electron pairs are oriented in space as far apart as possible. Molecular shapes predicted by Sidgwick-Powell theory have been summarised in Table 2.4.

Table 2.4 Molecular Shapes Predicted By Sidgwick-Powell Theory

| Number of electron-pairs in outer-shell | Shapes of molecules                                                                                    | Bond angles  |
|-----------------------------------------|--------------------------------------------------------------------------------------------------------|--------------|
| 2                                       | Linear              | 180°         |
| 3                                       | Plane triangle      | 120°         |
| 4                                       | Tetrahedron         | 109° 28'     |
| 5                                       | Trigonal bipyramid  | 120° and 90° |

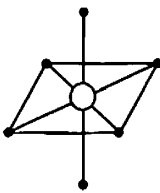
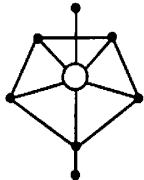
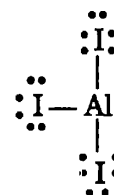
| Number of electron-pairs in outer-shell | Shapes of molecules                                                                                        | Bond angles |
|-----------------------------------------|------------------------------------------------------------------------------------------------------------|-------------|
| 6                                       | Octahedron              | 90°         |
| 7                                       | Pentagonal bipyramidal  | 72° and 90° |

**Illustration 2** Draw the Lewis structure for aluminium tri-iodide ( $\text{AlI}_3$ ).

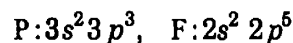
**Solution** The outer-shell electron configuration of Al is  $3s^2 3p^1$ . The Al atom forms three covalent bonds with the I atoms as follows :



We find that the octet rule is satisfied for the I atom, there are only six valence electrons around Al atom. The molecule is an example of the **incomplete octet**. Thus,  $\text{AlI}_3$  is a Lewis acid—an electron pair acceptor.

**Illustration 3** Draw the Lewis structure for  $\text{PF}_5$  in which all five F atoms are bonded directly to P atom.

**Solution** The outer-shell electron configuration for



Total number of valence electrons =  $7 \times 5 + 5 = 40$

P is a third-period element and it can have an expanded octet. The Lewis structure of  $\text{PF}_5$  is

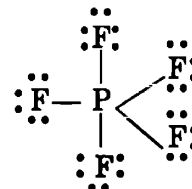
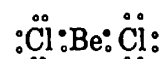
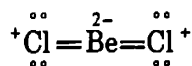


**Illustration 4** In the vapour phase, beryllium chloride consists of discrete  $\text{BeCl}_2$  molecules. Is the octet rule satisfied for Be in the compound. If not, can you form an octet around Be by drawing another resonance structure? How plausible is this structure?

**Solution** In single unit, octet of Be is short of four electrons.



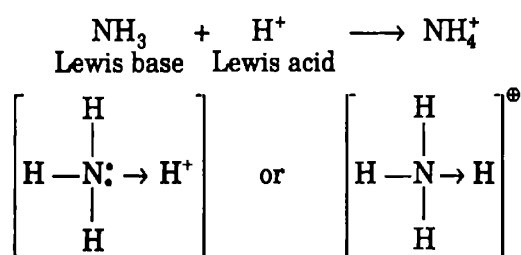
Octet around Be is formed in the following resonance structure but it is not plausible.



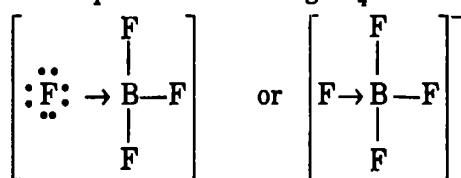
## Coordinate Bonding

A covalent bond results from the sharing of pair of electrons between two atoms where each atom contributes one electron to the bond. It is also possible to have an electron pair bond where both electrons originate from one atom and none from the other. Such bonds are called **coordinate bonds** or **dative bonds**. Since in coordinate bonds, two electrons are shared by two atoms, they differ from normal covalent bonds only in the way they are formed, and once formed they are identical to normal covalent bonds.

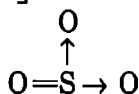
- It is represented as :  $\rightarrow$
- Atom/ion/molecule donating electron pair is called **DONOR** or **LEWIS BASE**
- Atom/ion/molecule accepting electron pair is called **ACCEPTOR** or **LEWIS ACID**; ( $\rightarrow$ ) points donor to acceptor.
- $\text{NH}_4^+$  :  $\text{NH}_3$  has three (N—H) bonds and one lone pair on N-atom. In  $\text{NH}_4^+$  formation this lone pair is donated to  $\text{H}^+$  (having no electron)



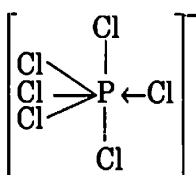
- $\text{BF}_4^-$  : In  $\text{BF}_3$ , B has incomplete octet.  $\text{F}^-$  can donate its one of the lone pairs to B forming  $\text{BF}_4^-$



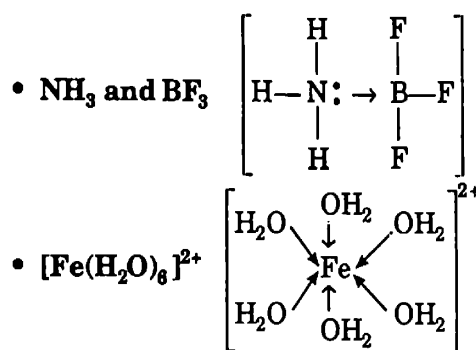
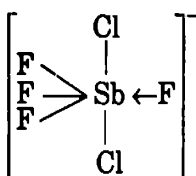
•  $\text{SO}_3$



•  $\text{PCl}_6^-$



•  $\text{SbF}_6^-$



Properties of the coordinate compounds are intermediates of ionic and covalent compounds. A comparison is summarised in Table 2.5.

Table 2.5 Comparison of Ionic, Covalent and Coordinate Compounds

|                                                          | Ionic                                                            | Covalent                                   | Coordinate            |
|----------------------------------------------------------|------------------------------------------------------------------|--------------------------------------------|-----------------------|
| (1) Binding force                                        | between ions strong (coulombic)                                  | between molecules smaller (van der Waals') | in between            |
| (2) m.p./b.p.                                            | high                                                             | less than ionic                            | in between            |
| (3) Conduction                                           | conductor of electricity in fused state and in aqueous solution. | of bad conductor                           | greater than covalent |
| (4) Solubility in polar solvent ( $\text{H}_2\text{O}$ ) | high                                                             | less                                       | in between            |
| (5) Solubility in non polar solvents (ether)             | low                                                              | high                                       | in between            |
| (6) Physical state                                       | generally solid                                                  | liquid and gas                             | solid, liquid, gas    |

**Illustration 1** Classify the following bonds as ionic, polar covalent or covalent, and give your reasons :

- SiSi bond in  $\text{Cl}_3\text{SiSiCl}_3$
- SiCl bond in  $\text{Cl}_3\text{SiSiCl}_3$
- CaF bond in  $\text{CaF}_2$
- NH bond in  $\text{NH}_3$

**Solution** (a) Covalent due to identical electronegativity.

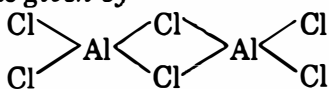
(b) One electrons pair is shared between Si and Cl and thus, covalent bond is expected but electronegativity of Cl is greater than that of Si and some polarity develops giving polar-covalent nature.

(c) Ionic since Ca completes its octet by transfer of two outer-shell electrons and two F atoms gain these two electrons thus, completing their octets



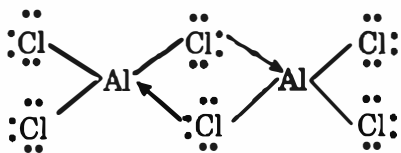
(d) Polar covalent, explanation as in (b).

**Illustration 2** In the gas phase, aluminium chloride exists as a dimer (a unit of two) with the formula  $\text{Al}_2\text{Cl}_6$ . Its skeletal structure is given by



Complete the Lewis structure and indicate the coordinate covalent bonds in the molecule.

**Solution**



## Formal Charge

The formal charge of an atom in a molecule is the hypothetical charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms in the bond. Formal charge ( $F$ ) is determined using

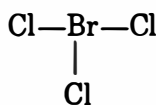
$$F = v - \frac{s}{2} - u$$

where,  $v$  = valence electrons

$s$  = shared electrons (forming bonds)

$u$  = unshared electrons

• In  $\text{BrCl}_3$



|    | $v$ | $s$ | $u$ | Formal charge |
|----|-----|-----|-----|---------------|
| Br | 7   | 6   | 4   | 0             |
| Cl | 7   | 2   | 6   | 0             |

• In  $\text{ICl}_4^-$

|    | $v$ | $s$ | $u$           | Formal charge |
|----|-----|-----|---------------|---------------|
| I  | 7   | 8   | 4 (one extra) | -1            |
| Cl | 7   | 2   | 6             | 0             |

• In  $\text{NH}_4^+$

|   | $v$ | $s$ | $u$ | Formal charge |
|---|-----|-----|-----|---------------|
| N | 5   | 8   | 0   | +1            |
| H | 1   | 2   | 0   | 0             |

- In many cases, we can draw more than one structure for a molecule, with different arrangement of atoms. We can use the following guidelines involving formal charge to decide between two or more possible structures for a molecule or ion :

### DEEP Focus

- A molecular structure that gives a Lewis structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
- If the Lewis structure must have non-zero formal charges, the structure with the lowest number of non-zero formal charge is preferable and a Lewis

structure with no more than one large formal charge ( $-2$ ,  $+2$  and so on) is preferable to a structure with several formal charges.

- Lewis structure should have adjacent formal charges of zero or of opposite sign.
- When we must choose among several Lewis structures with similar distribution of formal charges on the more electronegative atom is preferable.

Thiocyanate ion can be assigned three structures :

|                                                                    | Formal charges |    |    | Total charge |
|--------------------------------------------------------------------|----------------|----|----|--------------|
|                                                                    | N              | C  | S  |              |
| I $[\text{:}\ddot{\text{N}}=\text{C}=\ddot{\text{S}}\text{:}]^-$   | -1             | 0  | 0  | -1           |
| II $[\text{:}\ddot{\text{C}}=\text{N}=\ddot{\text{S}}\text{:}]^-$  | +1             | -2 | 0  | -1           |
| III $[\text{:}\ddot{\text{C}}=\text{S}=\ddot{\text{N}}\text{:}]^-$ | -1             | -2 | +2 | -1           |

In all these cases total formal charge is  $-1$ . But we prefer structure I because it has the lowest number of atoms with non-zero formal charge [guideline (b)].

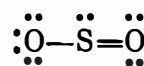
- Generally the most stable atomic skeleton is also that for which the sum of the electronegativity differences of adjacent atoms is maximum. Thus, for the arrangements  $\text{HOCl}$  and  $\text{HClO}$ , the electronegativities of the atoms yield :

$$\begin{array}{ccc} 2.2 & 3.44 & 3.16 \\ \text{H} & -\text{O}- & \text{Cl}; \end{array} \quad \Sigma = (3.44 - 2.20) + (3.44 - 3.16) = 1.52$$

$$\begin{array}{ccc} 2.2 & 3.16 & 3.44 \\ \text{H} & -\text{Cl}- & \text{O}; \end{array} \quad \Sigma = (3.16 - 2.20) + (3.44 - 3.16) = 1.24$$

Thus,  $\text{H}-\text{O}-\text{Cl}$  is the most stable structure. This is also consistent with formal charge distribution and Pauling's electroneutrality principle: in a molecule, electrons are so distributed that the residual charge on each atom becomes zero or nearly zero; hydrogen and the most electropositive metals may acquire partial positive charge and the most electronegative atom may acquire the negative charge.

**Illustration 1** Calculate the formal charge on each atom in the following electron-dot structure for  $\text{SO}_2$  :

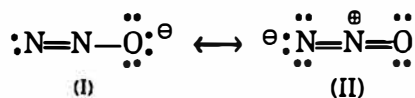


**Solution** Let  $v$  = valence electrons,  $F$  = formal charge,  $s$  = shared electrons,  $u$  = unshared electrons.

| Atom                 | $v$ | $s$ | $u$ | $F = v - \frac{s}{2} - u$ |
|----------------------|-----|-----|-----|---------------------------|
| Sulphur              | 6   | 6   | 2   | +1                        |
| Single-bonded oxygen | 6   | 2   | 6   | -1                        |
| Double-bonded oxygen | 6   | 4   | 4   | 0                         |



**Illustration 2** We can write two electron-dot structures for  $N_2O$ , one of which has a negative formal charge on the oxygen atom and the other of which has a negative formal charge on the terminal nitrogen atom.

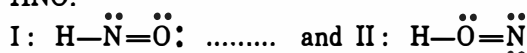


Which of the two electron-dot structures gives a more accurate representation of the molecule?

**Solution** Since oxygen is a more electronegative element than nitrogen, the structure that places a negative formal charge on oxygen is probably lower in energy than the structure that has a negative formal charge on nitrogen. Thus, (I) is more favourable than (II).

## Target Practice 1

1. Which one would better represent bonding in the molecule  $HNO$ ?



2. In each of the following Lewis structure, Z represents a main-group element. Name the group to which Z belongs in each case and give an example of a such a compound or ion that actually exists.



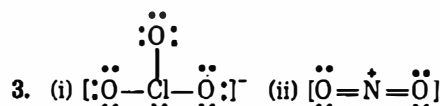
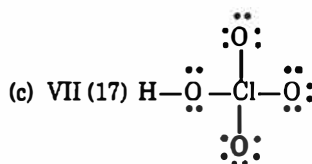
3. Draw Lewis structure for (i)  $\text{ClO}_3^-$  (chlorate ion) and (ii)  $\text{NO}_2^+$  (nitronium ion).



## Answers

1. I is better as octets of N and O are complete and duplet of H is also complete.

2. Group of Element Z Example



## Practice Exercise 1

1. Atomic number of the four elements A, B, C and D are respectively  $Z-1$ ,  $Z$ ,  $Z+1$  and  $Z+2$ . If  $Z=9$ , what is type of bonding between :

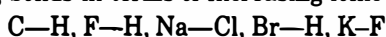
- (a) A and D (b) B and D  
(c) A and A (d) B and B

2. Valence electrons in the elements X and Y are 3 and 6. What is the formula of the compound formed from X and Y?

3. Classify Lewis acid and Lewis base out of:

- (a)  $\text{H}_2\text{O}$  (b)  $\text{NH}_3$   
(c)  $\text{H}^+$  (d)  $\text{BF}_3$   
(e)  $\text{AlH}_3$  (f)  $\text{ROH}$   
(g)  $\text{CH}_3\text{NH}_2$  (h)  $\text{CN}^-$   
(i)  $^+\text{CH}_3$

4. Use your knowledge of electronegativities, to arrange the following bonds in terms of increasing ionic character



5. Represent each of the following ionic compounds by an appropriate Lewis structures

- (a)  $\text{KIO}_3$   
(b)  $\text{Ca}(\text{OCl})_2$   
(c)  $\text{NH}_4\text{ClO}_4$

6. Propose Lewis structures for the following ionic species containing sulphur-to-sulphur bonds

- (a)  $\text{S}_2^{2-}$  (b)  $\text{S}_3^{2-}$   
(c)  $\text{S}_4^{2-}$  (d)  $\text{S}_5^{2-}$

7. Explain the formation of following compounds

- (a)  $\text{CaO}$  (b)  $\text{Mg}_3\text{N}_2$

8. Which of the following atoms would be expected to form negative ions and which would be expected to form positive ions in binary ionic compounds?

- (a) P, I, Mg, Cl, In, Cs, O, Pb, Co  
(b) Ca, Br, Na, N, F, Al, Sn, S, Cd

9. Calculate the lattice energy of a salt MX (s) from the data given below :

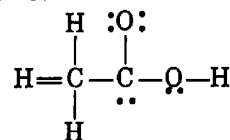
- Heat of formation of MX  $(\Delta H) = -550 \text{ kJ mol}^{-1}$   
Heat of sublimation of M  $(S) = 80 \text{ kJ mol}^{-1}$   
Heat of dissociation of  $\text{X}_2$   $(D) = 155 \text{ kJ mol}^{-1}$   
Ionisation energy of M  $(I) = 374 \text{ kJ mol}^{-1}$   
Electron affinity of X  $(E) = -343 \text{ kJ mol}^{-1}$

10. Arrange the following in increasing lattice energy :

- (a)  $\text{BeCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{BaCO}_3$   
(b)  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$

- (c) LiCl, NaCl, KCl  
(d) LiF, LiBr, LiI
11. The lattice energy of CaO (s) is  $-3460 \text{ kJ mol}^{-1}$ ; the lattice energy of  $\text{K}_2\text{O}$  is  $-2240 \text{ kJ mol}^{-1}$ . Account for this difference.
12. Specify which compound in the following pairs of ionic compounds has the higher lattice energy?  
(a) KCl or MgO (b) LiF or LiBr  
(c)  $\text{Mg}_3\text{N}_2$  or NaCl
13. Bond length can be calculated by merely adding covalent bond radii which are  $\text{H} = 0.28 \text{ \AA}$ ,  $\text{C} = 0.77 \text{ \AA}$ ,  $\text{N} = 0.70 \text{ \AA}$ ,  $\text{O} = 0.66 \text{ \AA}$ ,  $\text{Cl} = 0.99 \text{ \AA}$ ,  $(\text{C}=\text{C}) = 0.67 \text{ \AA}$ ,  $(\text{C}\equiv\text{C}) = 0.61 \text{ \AA}$ ,  $(\text{N}\equiv\text{N}) = 0.55 \text{ \AA}$ . Calculate bond lengths in:  
(a)  $\text{NH}_3$  (b)  $\text{CH}_2\text{Cl}_2$   
(c) HOCl (d) HCN  
(e)  $\text{CH}_2=\text{CH}_2$  (f)  $\text{CH}\equiv\text{CH}$
14. In which molecule is the van der Waals' force likely to be the most important in determining the melting point and boiling point?  
 $\text{ICl}$ ,  $\text{Br}_2$ ,  $\text{HCl}$ ,  $\text{H}_2\text{S}$ ,  $\text{CO}$
15. Write Lewis structure of:  
(a)  $\text{C}_3^{4-}$  (b)  $\text{PF}_6^-$   
(c)  $\text{ICl}_4^-$
16. The chlorine-to-oxygen bond distance in  $\text{ClO}_4^-$  is  $1.44 \text{ \AA}$ . What do you conclude about the structure of this ion?
17. Show that by using an expanded octet for the sulphur atom in thionyl chloride ( $\text{SOCl}_2$ ), you can write a Lewis structure with no formal charge.
18. Write Lewis structures for the following molecules:  
(a)  $\text{H}_2\text{NOH}$  (b)  $\text{N}_2\text{F}_2$   
(c) HONO (d)  $\text{H}_2\text{NNO}_2$
19. The skeletal structure of acetic acid shown below is correct, but some of the bonds are wrong.

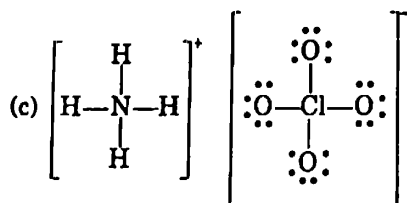
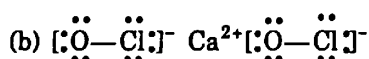
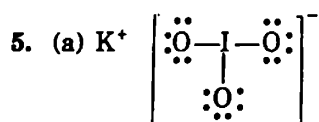
- (a) Identify the incorrect bonds and explain what is wrong with them  
(b) Write the correct Lewis structure.



20. Give an example of an ion or molecule containing Al that  
(a) obeys the octet rule  
(b) has an expanded octet  
(c) has an incomplete octet
21. Why does  $\text{NH}_3$  forms coordination complexes, whereas the isoelectronic species  $\text{CH}_4$  does not?
22.  $\text{PF}_3$  can act as a donor molecule while  $\text{NF}_3$  shows little tendency to act as a donor. Account for this observation.
23. Indicate the coordinate covalent bond (or bonds) in the product:  
(a)  $\text{Al}^{3+} + 6\text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_6^{3+} + 6\text{H}^+$   
(b)  $\text{CO} + \text{BF}_3 \longrightarrow \text{OCBF}_3$   
(c)  $\text{Sn}^{2+} + 3\text{Cl}^- \longrightarrow \text{SnCl}_3^-$   
(d)  $\text{H}_2\text{O} + \text{H}^+ \longrightarrow \text{H}_3\text{O}^+$   
(e)  $\text{SO}_3 + \text{O}^{2-} \longrightarrow \text{SO}_4^{2-}$
24. Write structures of the following indicating coordinate bonds wherever exist:  
(a)  $\text{N}_2\text{O}$  (b)  $\text{Cr}_2\text{O}_7^{2-}$   
(c)  $\text{CrO}_5$  (d)  $\text{Al}_2\text{Cl}_6$   
(e)  $\text{H}_3\text{PO}_4$  (f)  $\text{H}_3\text{PO}_3$   
(g)  $\text{H}_3\text{PO}_2$  (h)  $\text{NO}_2$
25. For each of the following pairs of elements, state whether the binary compound they form is likely to be ionic or covalent.  
(a) B and F (b) K and Br

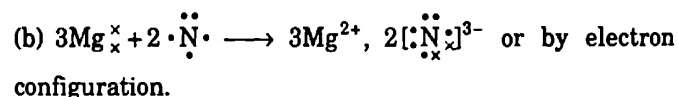
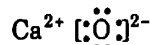
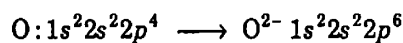
## Answers

1. (a) Ionic (b) Ionic (c) Covalent (d) Covalent  
2.  $\text{X}_2\text{Y}_3$   
3. Lewis acid : (c), (d), (e), (i); Lewis base : (a), (b), (f), (g), (h)  
4.  $\text{C}-\text{H} < \text{Br}-\text{H} < \text{F}-\text{H} < \text{Na}-\text{Cl} < \text{K}-\text{F}$



6. (a)  $[\text{:}\ddot{\text{S}}\text{---}\ddot{\text{S}}\text{:}]^{2-}$  similarly others.

7. (a)  $\text{Ca}:[\text{Ar}] 4s^2 \longrightarrow \text{Ca}^{2+} [\text{Ar}]$



8. Refer Table 2.1

9.  $-738.5 \text{ kJ mol}^{-1}$

10. (a)  $\text{BaCO}_3 < \text{SrCO}_3 < \text{CaCO}_3 < \text{MgCO}_3 < \text{BeCO}_3$



11.  $\text{K}^+ > \text{Ca}^{2+}$  (size),  $\text{K}^+ < \text{Ca}^{2+}$  (charge)

$\text{O}^{2-}$  is identical, polarising power of  $\text{K}^+ < \text{Ca}^{2+}$  thus,  $\text{K}_2\text{O}$  is more ionic than  $\text{CaO}$  thus, lattice energy of  $\text{CaO} > \text{K}_2\text{O}$ .

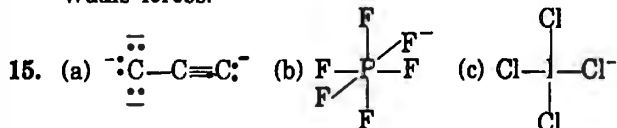
12. (a) MgO (b) LiF (c)  $\text{Mg}_3\text{N}_2$

13. (a) N—H 0.98 Å (b) C—Cl 1.76 Å  
C—H 1.05 Å

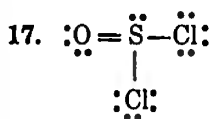
- (c) O—H 0.94 Å (d) H—C 1.05 Å  
O—Cl 1.65 Å C≡N 1.16 Å

- (e) C—H 1.05 Å (f) C—H 1.05 Å  
C=C 1.34 Å C=C 1.22 Å

14.  $\text{Br}_2$ , other molecules have a dipole in addition to van der Waals' forces.



16. There must be considerable double bond character in the bonds.

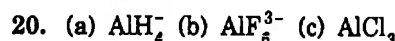
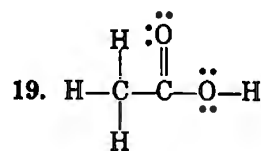
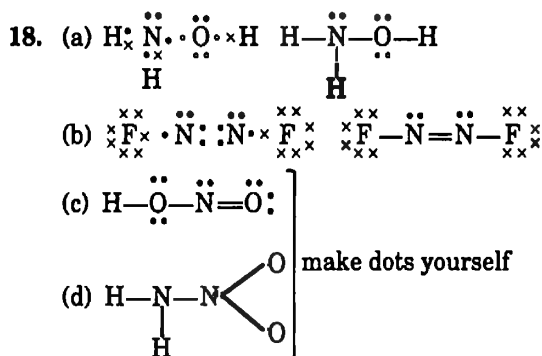


$$\text{Formal charge} = \frac{\text{valence electrons} - \text{bonding electrons}}{2} - \text{lone pair electrons}$$

$$\text{Oxygen} = 6 - \frac{4}{2} - 4 = 0$$

$$\text{Sulphur} = 6 - \frac{8}{2} - 2 = 0$$

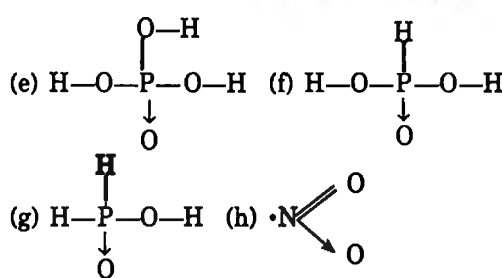
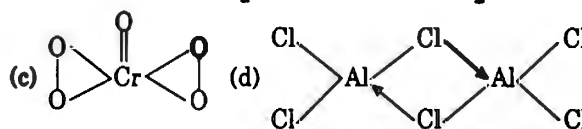
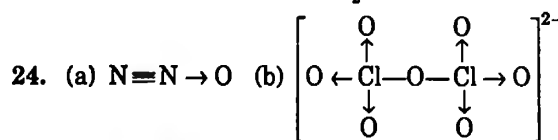
$$\text{Chlorine} = 7 - \frac{2}{2} - 6 = 0$$



21. Due to lone-pair on N

22. In  $\text{PF}_3$  lone-pair on P is easily donated compared to that of N.

23. Lewis bases (donor) are  $\text{H}_2\text{O}$  ( $\text{OH}^-$ ),  $\text{CO}$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{O}^{2-}$



25. (a) Covalent (b) Ionic

## Valence Shell Electron Pair Repulsion (VSEPR) Theory (Gillespie Theory)

- The shape of the molecule is determined by repulsions between all of the electron pairs present in the valence shell.
- There can be
  - (lone pair–lone pair)
  - (lone pair–bond pair)
  - (bond pair–bond pair) repulsions.
- Repulsion is in order
 
$$(lp - lp) > (lp - bp) > (bp - bp)$$
- The magnitude of repulsion between pairs of electrons depends on the electronegativity difference between the central atom and the other atom.
- Double bonds cause more repulsion than single bonds, and triple bonds cause more repulsion than a double bond.
- From the Table 2.6, it is quite evident that presence of lone pair will change geometry of the molecule (which is not shown in Table 2.4).

### DEEP Focus

To find which geometry applies, we determine the **Steric number**,  $S_N$ , of the central atom, which is defined as

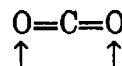
$$S_N = \left( \text{Number of atom bonded to central atom} \right) + \left( \text{Number lone pair on central atom} \right)$$

The steric number is used to predict molecular geometries. If there are no lone pairs on the central atom then

$$S_N = \text{number of atoms bonded to central atom} = n$$

There is no repulsion and geometry is retained when lone-pairs are present, the situation changes slightly due to various types of repulsion as shown. Double-bonded or triple-bonded atoms count the same as single-bonded atoms in determining the steric number.

In  $\text{CO}_2$ , two double-bonded oxygen atoms are attached to central carbon and there are no lone pairs on that atom, thus  $S_N = 2$



Consider this double-bonded atom as single atom.



## Effect of Electronegativity

$\text{NF}_3$  and  $\text{NH}_3$  both have structures based on tetrahedron with one corner occupied by a lone pair. The high electronegativity of F pulls the bonding electrons further away from N than in  $\text{NH}_3$ . Thus, repulsion between bond pairs is less in  $\text{NF}_3$  than  $\text{NH}_3$ . Hence, the

lone pair in  $\text{NF}_3$  causes a greater distortion from tetrahedral and gives a  $\text{F—N—F}$  bond angles of  $102^\circ 30'$  compared with  $107^\circ 48'$  in  $\text{NH}_3$ . The same effect is found in  $\text{H}_2\text{O}$  (bond angle  $104^\circ 27'$ ) and  $\text{F}_2\text{O}$  (bond angle  $102^\circ$ ) and also in  $\text{H}_2\text{O}$  (bond angle  $104^\circ 27'$ ) and  $\text{H}_2\text{S}$  (bond angle  $90^\circ$ ).

Table 2.6 The Effect of Bonding and Lone Pairs on Geometry and Bond Angles

| Example                                              | Orbitals on central atom | Theoretical shape      | Number of  |            |                         | $S_N$ | Bond angle                         | Distorted geometry due to repulsion |
|------------------------------------------------------|--------------------------|------------------------|------------|------------|-------------------------|-------|------------------------------------|-------------------------------------|
|                                                      |                          |                        | Bond pairs | Lone pairs | VSEPR notation          |       |                                    |                                     |
| $\text{BeCl}_2$                                      | 2                        | Linear                 | 2          | 0          | $\text{AX}_2$           | 2     | $180^\circ$                        | Linear                              |
| $\text{BF}_3$                                        | 3                        | Plane triangle         | 3          | 0          | $\text{AX}_3$           | 3     | $120^\circ$                        | Plane triangle                      |
| $\text{SO}_2$                                        | 3                        | Plane triangle         | 2          | 1          | $\text{AX}_2\text{E}$   | 3     | $119^\circ$                        | Angular                             |
| $\text{CH}_4, \text{SiH}_4$                          | 4                        | Tetrahedral            | 4          | 0          | $\text{AX}_4$           | 4     | $109^\circ 28'$                    | Tetrahedral                         |
| $\text{NH}_3$                                        | 4                        | Tetrahedral            | 3          | 1          | $\text{AX}_3\text{E}$   | 4     | $107^\circ 48'$                    | Trigonal pyramidal                  |
| $\text{NF}_3$                                        | 4                        | Tetrahedral            | 3          | 1          | $\text{AX}_3\text{E}$   | 4     | $102^\circ 35'$                    | Pyramidal                           |
| $\text{H}_2\text{O}$                                 | 4                        | Tetrahedral            | 2          | 2          | $\text{AX}_2\text{E}_2$ | 4     | $104^\circ 27'$                    | Angular                             |
| $\text{F}_2\text{O}$                                 | 4                        | Tetrahedral            | 2          | 2          | $\text{AX}_2\text{E}_2$ | 4     | $102^\circ$                        | Angular                             |
| $\text{H}_2\text{S}$                                 | 4                        | Tetrahedral            | 2          | 2          | $\text{AX}_2\text{E}_2$ | 4     | $90^\circ$                         | Angular                             |
| $\text{PCl}_5$                                       | 5                        | Trigonal bipyramidal   | 5          | 0          | $\text{AX}_5$           | 5     | $120^\circ$ and $90^\circ$         | Trigonal bipyramidal                |
| $\text{XeO}_2\text{F}_2, \text{SF}_4, \text{IF}_4^+$ | 5                        | Trigonal bipyramidal   | 4          | 1          | $\text{AX}_4\text{E}$   | 5     | $101^\circ 36'$ and $86^\circ 33'$ | Irregular tetrahedral               |
| $\text{ClF}_3$                                       | 5                        | Trigonal bipyramidal   | 3          | 2          | $\text{AX}_3\text{E}_2$ | 5     | $87^\circ 40'$                     | T-shaped                            |
| $\text{I}_3, \text{XeF}_2$                           | 5                        | Trigonal bipyramidal   | 2          | 3          | $\text{AX}_2\text{E}_3$ | 5     | $180^\circ$                        | Linear (also see text)              |
| $\text{SF}_6$                                        | 6                        | Octahedral             | 6          | 0          | $\text{AX}_6$           | 6     | $90^\circ$                         | Octahedral                          |
| $\text{XeOF}_4, \text{BrF}_5$                        | 6                        | Octahedral             | 5          | 1          | $\text{AX}_5\text{E}$   | 6     | $84^\circ 30'$                     | Square pyramidal                    |
| $\text{ICl}_4^-, \text{XeF}_4$                       | 6                        | Octahedral             | 4          | 2          | $\text{AX}_4\text{E}_2$ | 6     | $90^\circ$                         | Square planar                       |
| $\text{IF}_7$                                        | 7                        | Pentagonal bipyramidal | 7          | 0          | $\text{AX}_7$           | 7     | $72^\circ, 90^\circ$               | Pentagonal bipyramidal              |

E stands for lone pair.

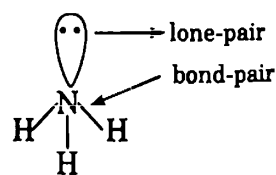
## Isoelectronic Principle

Isoelectronic species usually have the same structure. This may be extended to species with the same number of valence electrons.

| Species                                        | Steric number | Structures           |
|------------------------------------------------|---------------|----------------------|
| $\text{CH}_4, \text{NH}_4^+, \text{BF}_4^-$    | 4             | Tetrahedral          |
| $\text{CO}_3^{2-}, \text{NO}_3^-, \text{SO}_3$ | 3             | Planar triangle      |
| $\text{CO}_2, \text{N}_3^-, \text{NO}_2^+$     | 2             | Linear               |
| $\text{PCl}_5$                                 | 5             | Trigonal bipyramidal |
| $\text{SF}_6$                                  | 6             | Octahedral           |

## Applications

(a) **Ammonia ( $\text{NH}_3$ )** There are ( $lp - bp$ ) and ( $bp - bp$ ) repulsions. The steric number is 4, and the electron pairs arrange

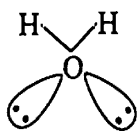


themselves into an approximately tetrahedral structure. The lone-pair is not identical to three bonding pairs, however, so there is no reason for the electron pair structure to be exactly tetrahedral. It is found that lone pair tends to occupy more space than bonding pairs hence bond angles are reduced to  $107^\circ 48'$  and structure is pyramidal.

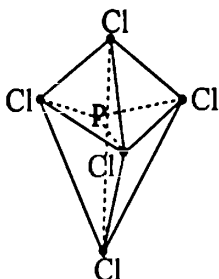
## DEEP Focus

The presence of the lone pair causes slight distortion from  $109^\circ 28'$  to  $109^\circ 28'$  to  $104^\circ 27'$ .

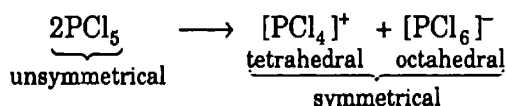
- (b) **Water ( $\text{H}_2\text{O}$ )** : There are two bond pairs and two lone pairs. Presence of two lone pairs distorts the bond angle from  $109^\circ 28'$  to  $104^\circ 27'$ .



- (c) **Phosphorus pentachloride ( $\text{PCl}_5$ )** : There is no lone pair so the structure is not distorted. However, a trigonal bipyramidal is not a completely regular structure, since some bond angles are  $90^\circ$  and others  $120^\circ$ .

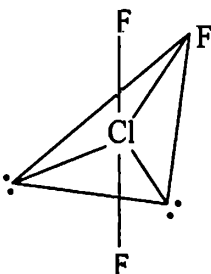


Symmetrical structures are usually more stable than asymmetrical ones. Thus,  $\text{PCl}_5$  is highly unstable, and in the solid state it splits into  $[\text{PCl}_4]^+$  and  $[\text{PCl}_6]^-$  ions.



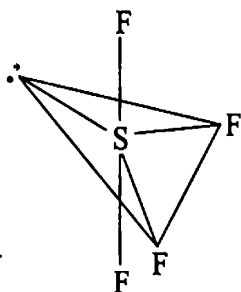
- (d) **Chlorine trifluoride ( $\text{ClF}_3$ )**

There are three bond pairs and two lone pairs. As a general rule, if lone pairs occur in a trigonal bipyramidal they will be located in the equatorial positions (round the middle) rather than the apical positions (top and bottom), since this arrangement minimises the repulsive forces.

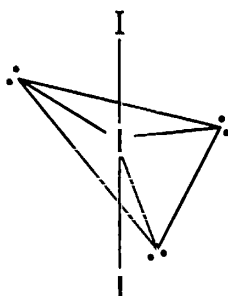


- (e) **Sulphur tetrafluoride ( $\text{SF}_4$ )**

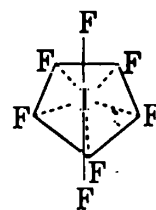
There are four bond pairs and one lone pair. To minimise the repulsive forces the lone pair occupies an equatorial position, and F atoms are located at the other four corners.



- (f) **Triiodide ion ( $\text{I}_3^-$ )**  $\text{I}_3^-$  ion is made up of an  $\text{I}_2$  molecule with an  $\text{I}^-$  bonded to it by means of a coordinate bond in which  $\text{I}_2$  is lone pair acceptor (Lewis acid) and  $\text{I}^-$  the lone pair donor (Lewis base). There are two bond pairs and three lone pairs in the outer-shell of central atom. To minimise the repulsive forces the three lone pairs occupy the equatorial position. The ion is therefore linear in shape with a bond angle of exactly  $180^\circ$ .



- (g) **Iodine heptafluoride ( $\text{IF}_7$ )** This is the only common example of a non-transition element using seven orbitals for bonding giving a pentagonal bipyramid.



- (h)  **$\text{ClO}_3^+$**  The central chlorine atom

has all of its valence electrons (Cl loses one electron in the formation of  $\text{Cl}^+$ ) involved in bonds to three oxygen atoms and no lone pair exists. Steric number is three and structure is thus **trigonal planar**.

- (i)  **$\text{ClO}_2^+$**  Chlorine (being positively charged) has six valence electrons. Two pairs (in all four electrons) are involved in bonding with two oxygen atoms and thus one lone pair exists. Thus, steric number ( $2 + 1 = 3$ ) is three. The predicted geometry is bent with an angle some what less than  $120^\circ$ .

**Illustration 1** Use the VSEPR model to predict the geometry of the following

- (a)  $\text{AsH}_3$  (b)  $\text{OF}_2$  (c)  $\text{AlCl}_4^-$  (d)  $\text{C}_2\text{H}_4$  (e)  $\text{ClF}_2^+$

## Solution

| Species                    | Structure | Repulsion/angle                                                              | Geometry                                                                                                                                               |
|----------------------------|-----------|------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------|
| (a) $\text{AsH}_3$         |           | $lp - bp$<br>$bp - bp$<br>bond angle less than $109.5^\circ$                 | trigonal pyramidal                                                                                                                                     |
| (b) $\text{OF}_2$          |           | $lp - lp$<br>$lp - bp$<br>$bp - bp$<br>much less than that of $\text{AsH}_3$ | bent shape (like $\text{H}_2\text{O}$ ), since electronegativity of $\text{F} > \text{O}$ , hence bond angle is less than that of $\text{H}_2\text{O}$ |
| (c) $\text{AlCl}_4^-$      |           | $bp - bp$<br>(no lone pair)<br>$109.5^\circ$                                 | tetrahedral                                                                                                                                            |
| (d) $\text{C}_2\text{H}_4$ |           | $bp - bp$<br>(no lone pair)<br>$120^\circ$                                   | trigonal planar                                                                                                                                        |
| (e) $\text{ClF}_2^+$       |           | as in (b)                                                                    | angular                                                                                                                                                |

**Illustration 2** The triiodide ion ( $\text{I}_3^-$ ) in which the I atoms are arranged in a straight line is stable, but the corresponding  $\text{F}_3^-$  ion does not exist. Explain.

**Solution**  $\text{F}_3^-$  and  $\text{I}_3^-$  are of same group. I can expand its octet but F cannot and thus, in  $\text{I}_3^-$  octet rule is not violated, but in  $\text{F}_3^-$  octet rule is violated.

## Assessing Molecular Shape

### DEEP Focus

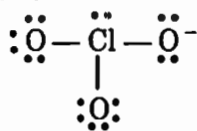
By use of VSEPR theory, we can decide the shape of the molecule based on four-step procedure.

- Draw a plausible Lewis structure of the species (molecule or polyatomic ion)
- Determine the number of electron pairs around the central atom and identify each pair as being either a bond-pair or a lone pair.
- Establish the geometrical orientation of the electron pairs around the central atom (linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral).
- Use the positions around the central atom that are occupied by other atoms (not lone-pair electrons) to specify the geometrical shape using Table 2.6.

#### $\text{ClO}_3^-$

- Number of valence electrons is  

|         |              |               |      |
|---------|--------------|---------------|------|
| from Cl | from O       | due to charge |      |
| 7       | $3 \times 6$ | +             | 1    |
|         |              |               | = 26 |
- Less electronegative atom is central atom in the Lewis structure. Thus, plausible structure is

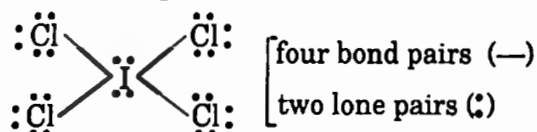


- There are three bond pairs (—) and one lone pair (.) on chlorine atom total being four.
- By Table 2.6, the orientation of four electron pairs is tetrahedral.
- In VSEPR notation the  $\text{ClO}_3^-$  ion is  $\text{AX}_3\text{E}$  (E stands for lone pair of electrons — Table 2.6). The ion has a pyramidal shape.

#### $\text{ICl}_4^-$

- Number of valence electrons  

|        |              |               |      |
|--------|--------------|---------------|------|
| from I | from Cl      | due to charge |      |
| 7      | $7 \times 4$ | +             | 1    |
|        |              |               | = 36 |
- I is the central atom being less electronegative and four Cl atoms around it.
- To complete octet, total electrons required = 32 that means four electrons are extra and lie on I atom as two lone pairs. Thus, plausible structure is



- By Table 2.6, the orientation of six electron-pairs around the central atom is octahedral.
- The  $\text{ICl}_4^-$  anion is of the type  $\text{AX}_4\text{E}_2$  and thus, it is square planar.

## Sigma and Pi Bonds

There can be following types of overlapping along the axes (end to end) :



Fig. 2.1 Sigma overlap (lobes point along nuclei)

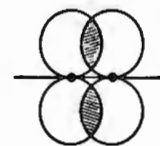
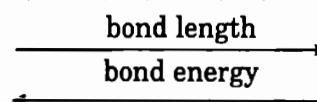
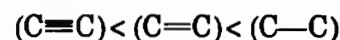


Fig. 2.2 Pi overlap (lobes are at right angles to the line joining the nuclei)

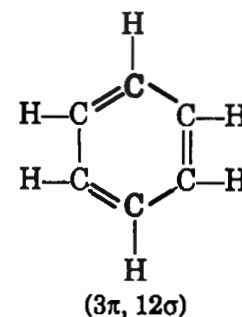
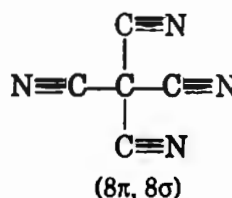
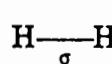
- (s – s) overlapping when s-orbital overlaps with another s-orbital
- (s – p) overlapping, (p can be  $p_x$  or  $p_y$  or  $p_z$ )
- ( $p_x$  –  $p_x$ ) overlapping
- any of the hybrid orbitals overlaps with another hybrid orbital or s or p orbital. (to be taken later)

Bond formed in this manner is called **sigma ( $\sigma$ ) bond** in which electron density is concentrated in between the two atoms, and on a line joining the two atoms.

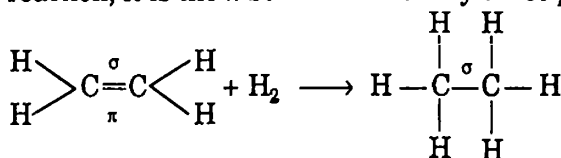
- Double or triple bonds occur by sideways overlap of orbitals (like ( $p_y$  –  $p_y$ ) and ( $p_z$  –  $p_z$ ) orbitals) giving pi ( $\pi$ ) bonds in which electron density also concentrates between the atoms, but on either side of the line joining the atoms.
- The shape of the molecule is determined by the  $\sigma$ -bonds (and lone pairs) but not by the  $\pi$  bonds. Pi bonds merely shorten bond length. Thus,



- If only single bonds exist in a molecule, all will be of  $\sigma$  type. In a double bond, one will be  $\sigma$  and the other  $\pi$  type while in a triple bond, one will be  $\sigma$  and other two  $\pi$ .



- In a reaction, it is the  $\pi$  bond that actually takes part

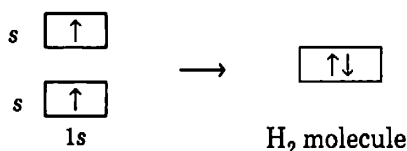


Thus,  $\pi$ -bond is more reactive than  $\sigma$  bond.

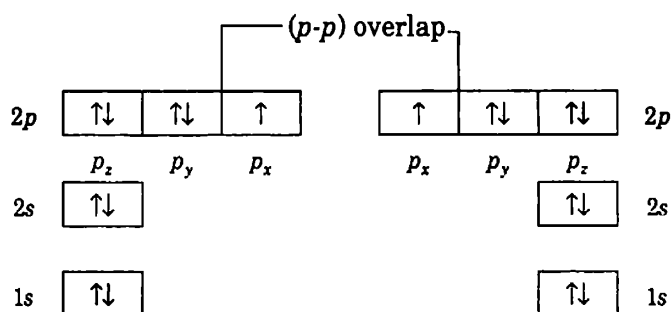
## Valence Bond Theory

The covalent bond is a region of high electron charge-density (high electron-probability) that results from the overlap of atomic orbitals between two atoms. In general, the greater the amount of overlap between two orbitals, the stronger the bond. For each bond there is a condition of maximum atomic orbital overlap leading to maximum bond strength at a particular internuclear distance (bond length). This is called **Valence Bond Approach**.

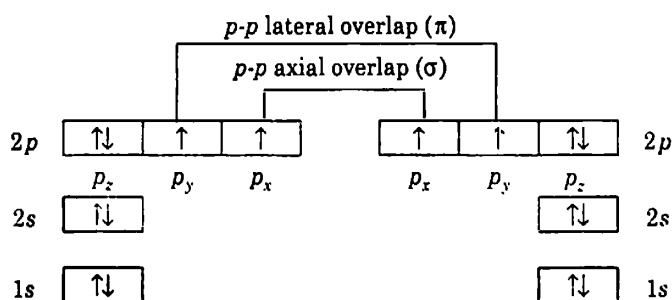
- This is a localised electron model of bonding.
- Most of the electrons retain the same orbital locations as in a separated atoms, and the bonding electrons are localised (fixed) in the region of atomic orbital overlap.
- In  $\text{H}_2$  molecules,  $\text{H}-\text{H}$   $\sigma$  bond is by  $s-s$  overlapping



- In  $\text{F}_2$  molecule  $\text{F}-\text{F}$   $\sigma$  bond is by axial overlapping of two  $p$ -orbitals.



- In  $\text{O}_2$  molecule One  $\sigma$  bond is by axial overlap of  $p$ -orbitals and  $\pi$  bond is by lateral overlap of  $p$ -orbitals.



- In  $\text{N}_2$  molecule One  $\sigma$  bond is by axial overlap of  $p$ -orbitals and two  $\pi$  bonds are by lateral overlap of  $p$ -orbitals.

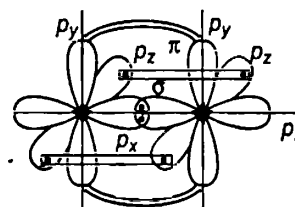
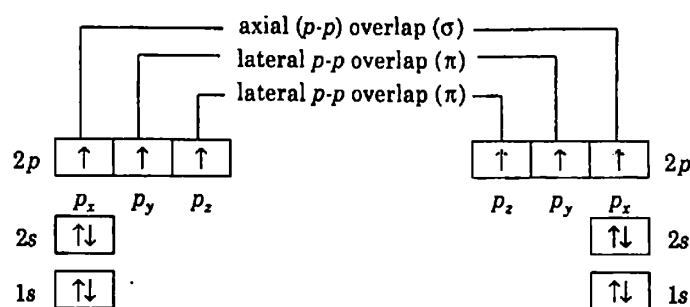
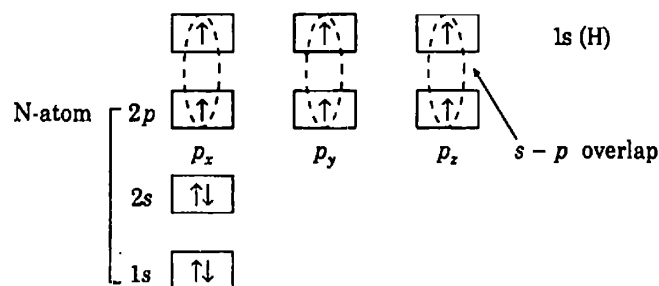


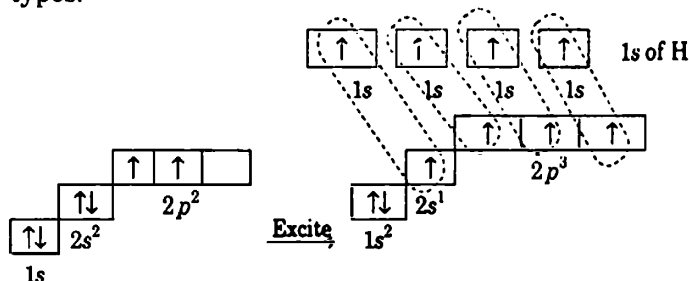
Fig. 2.3 Structure of  $\text{N}_2$  by valence bond method

- In  $\text{NH}_3$  : Three  $\sigma$  bonds are by ( $s-p$ ) overlap of H and N-atoms



## Hybridisation

We consider formation of  $\text{CH}_4$  molecule based on **valence bond approach**. To account for tetravalent nature of carbon, we take it in excited state in which there are four unpaired electrons and four  $\text{C}-\text{H}$   $\sigma$  bonds are supposed to be by overlap of  $s-s$ ,  $s-p_x$ ,  $s-p_y$  and  $s-p_z$  types.



### Ground state

### Excited state

What do you think about these ( $\text{C}-\text{H}$ ) bonds?

- are they equivalent?
  - are they having different bond lengths and bond energies (due to different types of overlap)?
- our answer is :
- they are equivalent;
  - they have equal bond energy and bond length.

This is due to formation of new orbitals before overlapping takes place, by a process called **Hybridization**.

**Hybridization is defined as the concept of intermixing of orbitals of same energy or of slightly different energy to produce entirely new orbitals of equivalent energy, identical shapes and symmetrically disposed in plane.** New orbitals formed are called **hybrid orbitals**.

- Only the orbitals of an isolated single atom can undergo Hybridization.
- The hybrid orbitals generated are equal in number to that of the pure atomic orbitals which mix up.
- A hybrid orbital, like the atomic orbitals, cannot have more than two electrons of opposite spins.

Hybrid orbitals do not make  $\pi$  bonds. If there are  $\pi$ -bonds, equal number of atomic orbitals must be left unhybridised for  $\pi$  bonding.

Number of orbitals and type of Hybridization have been summarised in Table 2.7.

## How to Determine the Type of Hybridization

For this, one needs to know first of all the numbers of lone pairs (by use of VSEPR theory). We adopt two methods for study of type of Hybridization :

**Method I :** Count number of atoms directly attached to central atom + lone pairs + single electrons

**Method II :** Count  $\sigma$  bonds +  $\rightarrow$  (coordinate) bonds + lone pairs + single electrons

This number comes out to be

2  $\Rightarrow$   $sp$  hybridization

3  $\Rightarrow$   $sp^2$  hybridization

4  $\Rightarrow$   $sp^3$  hybridization or  $dsp^2$  Hybridization

(decided by way of orbital used)

5  $\Rightarrow$   $sp^3d$  hybridization

6  $\Rightarrow$   $sp^3d^2$  hybridization or  $d^2sp^3$  hybridization

(based on outer  $d$  or inner  $d$ -orbitals are used).

We illustrate methods in Table 2.8.

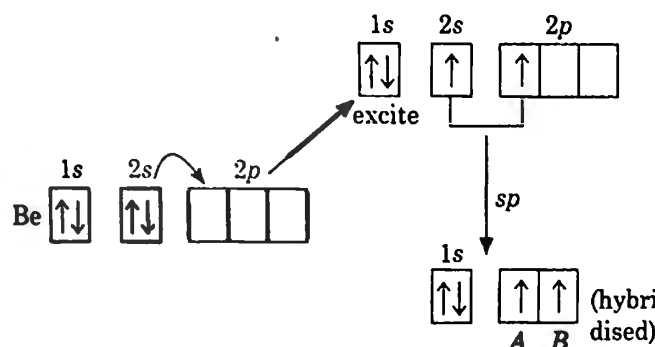
Table 2.7 Hybrid Orbitals and their Geometric Orientation

| Atomic orbitals (number)      | Hybrid orbitals (number) | Orientation        | Example                                                                                       | Predicted bond angle                                             | Actual shape (Refer table 2.6)                                                                                                |
|-------------------------------|--------------------------|--------------------|-----------------------------------------------------------------------------------------------|------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------|
| $s + p$ (two)                 | $sp$ (two)               | linear             | $\text{BeCl}_2, \text{CO}_2, \text{C}_2\text{H}_2$                                            | $180^\circ$                                                      | linear                                                                                                                        |
| $s + p + p$ (three)           | $sp^2$ (three)           | trigonal planar    | $\text{BF}_3, \text{C}_2\text{H}_4, \text{SO}_2, \text{SO}_3$                                 | $120^\circ$                                                      | trigonal planar                                                                                                               |
| $s + p + p + p$ (four)        | $sp^3$ (four)            | tetrahedral        | $\text{CH}_4$<br>$\text{NH}_3$<br>$\text{H}_2\text{O}$                                        | $109^\circ 28'$<br>$107^\circ 48'$<br>$104^\circ 27'$            | tetrahedral<br>trigonal pyramidal (due to $lp - bp$ repulsion)<br>angular (V-shaped) due to $lp - lp$ and $lp - bp$ repulsion |
| $s + p + p + p + d$ (five)    | $sp^3d$ (five)           | trigonal pyramidal | $\text{PCl}_5$<br>$\text{SF}_4$                                                               | $120^\circ$ and $90^\circ$<br>$101^\circ 36'$ and $86^\circ 33'$ | trigonal pyramidal<br>irregular tetrahedral                                                                                   |
| $s + p + p + p + d + d$ (six) | $sp^3d^2$ (six)          | octahedral         | $\text{I}_3^-$<br>$\text{SF}_6$<br>$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$<br>$\text{XeF}_4$ | $180^\circ$<br>$90^\circ$<br>$90^\circ$<br>$90^\circ$            | linear<br>octahedral<br>octahedral<br>square planar (with two lone pairs)                                                     |
| $d + d + s + p + p + p$ (six) | $d^2sp^3$ (six)          | octahedral         | $[\text{Fe}(\text{CN})_6]^{4-}$<br>$[\text{Co}(\text{NH}_3)_6]^{3+}$                          | $90^\circ$<br>$90^\circ$                                         | octahedral<br>octahedral                                                                                                      |
| $d + s + p + p$ (four)        | $dsp^2$ (four)           | square planar      | $[\text{Ni}(\text{CN})_4]^{2-}$<br>$[\text{Pt}(\text{NH}_3)_4]^{2+}$                          | $90^\circ$<br>$90^\circ$                                         | square planar<br>square planar                                                                                                |

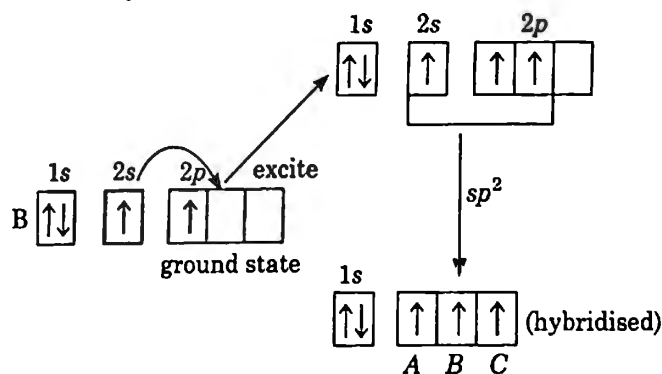
Table 2.8 Method of Determination of Type of Hybridization

| Molecule or Ion                                                                                                 | Central atom                     | Number of electrons attached to central atom |                    |          |                     |                         | Total hybrid orbitals |                           | Type      |
|-----------------------------------------------------------------------------------------------------------------|----------------------------------|----------------------------------------------|--------------------|----------|---------------------|-------------------------|-----------------------|---------------------------|-----------|
|                                                                                                                 |                                  | atoms (a)                                    | $\sigma$ bonds (b) | $lp$ (c) | single electron (d) | $\rightarrow$ bonds (e) | Method I (a + b + c)  | Method II (b + c + d + e) |           |
| $\text{H}-\text{Be}-\text{H}$                                                                                   | Be                               | 2                                            | 2                  | —        | —                   | —                       | 2                     | 2                         | $sp$      |
| $\begin{array}{c} \text{H} \\ \diagdown \\ \text{B}-\text{H} \\ \diagup \\ \text{H} \end{array}$                | B                                | 3                                            | 3                  | —        | —                   | —                       | 3                     | 3                         | $sp^2$    |
| $\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$                     | C                                | 4                                            | 4                  | —        | —                   | —                       | 4                     | 4                         | $sp^3$    |
| $\text{O}=\text{C}=\text{O}$                                                                                    | C                                | 2                                            | 2                  | —        | —                   | —                       | 2                     | 2                         | $sp$      |
| $\begin{array}{c} \text{H}-\text{C}=\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$      | C (any)                          | 3                                            | 3                  | —        | —                   | —                       | 3                     | 3                         | $sp^2$    |
| $\text{H}-\text{C}\equiv\text{C}-\text{H}$                                                                      | C (any)                          | 2                                            | 2                  | —        | —                   | —                       | 2                     | 2                         | $sp$      |
| $\begin{array}{c} \cdot\cdot \\   \\ \text{H}-\text{N}-\text{H} \\   \\ \text{H} \end{array}$                   | N                                | 3                                            | 3                  | 1        | —                   | —                       | 4                     | 4                         | $sp^3$    |
| $\begin{array}{c} \cdot\cdot \\   \\ \text{H}-\text{O}-\text{H} \\   \\ \cdot\cdot \end{array}$                 | O                                | 2                                            | 2                  | 2        | —                   | —                       | 4                     | 4                         | $sp^3$    |
| $\begin{array}{c} \text{Cl} \\   \\ \text{Cl}-\text{P}-\text{Cl} \\   \\ \text{Cl} \end{array}$                 | P                                | 5                                            | 5                  | —        | —                   | —                       | 5                     | 5                         | $sp^3d$   |
| $\begin{array}{c} \text{F} \\   \\ \text{F}-\text{S}-\text{F} \\   \\ \text{F} \end{array}$                     | S                                | 6                                            | 6                  | —        | —                   | —                       | 6                     | 6                         | $sp^3d^2$ |
| $\begin{array}{c} \text{O} \\ // \\ \text{N} \\ // \\ \text{O} \end{array}$                                     | N                                | 2                                            | 1                  | —        | 1                   | 1                       | 3                     | 3                         | $sp^2$    |
| $:\text{N}\equiv\text{N}:$                                                                                      | N (any)                          | 1                                            | 1                  | 1        | —                   | —                       | 2                     | 2                         | $sp$      |
| or $\begin{array}{c} \cdot\cdot \\   \\ \text{O}=\text{S}=\text{O} \\   \\ \cdot\cdot \end{array}$              | S                                | 2                                            | 1                  | 1        | —                   | 1                       | 3                     | 3                         | $sp^2$    |
| $\text{H}_3\text{C}-\overset{\text{O}}{\underset{\cdot\cdot}{\text{C}}}-\text{O}-\text{H}$                      | C                                | 3                                            | 3                  | —        | —                   | —                       | 3                     | 3                         | $sp^2$    |
| $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$                                                                   | C (any)                          | 3                                            | 3                  | —        | —                   | —                       | 3                     | 3                         | $sp^2$    |
| $\begin{array}{c} \text{O} \\   \\ \text{H}-\text{O}-\text{S}-\text{O}-\text{H} \\   \\ \text{O} \end{array}$   | S                                | 4                                            | 2                  | —        | —                   | 2                       | 4                     | 4                         | $sp^3$    |
| $\begin{array}{c} \text{O} \\    \\ \text{H}-\text{O}-\text{S}-\text{O}-\text{H} \\    \\ \text{O} \end{array}$ | S                                | 4                                            | 4                  | —        | —                   | —                       | 4                     | 4                         | $sp^3$    |
| $:\text{N}\equiv\text{N}::\ddot{\text{O}}:$                                                                     | N                                | 2                                            | 2                  | —        | —                   | —                       | 2                     | 2                         | $sp$      |
|                                                                                                                 | O                                | 1                                            | 1                  | 2        | —                   | —                       | 3                     | 3                         | $sp^2$    |
|                                                                                                                 | N <sub><math>\alpha</math></sub> | 1                                            | 1                  | 1        | —                   | —                       | 2                     | 2                         | $sp$      |

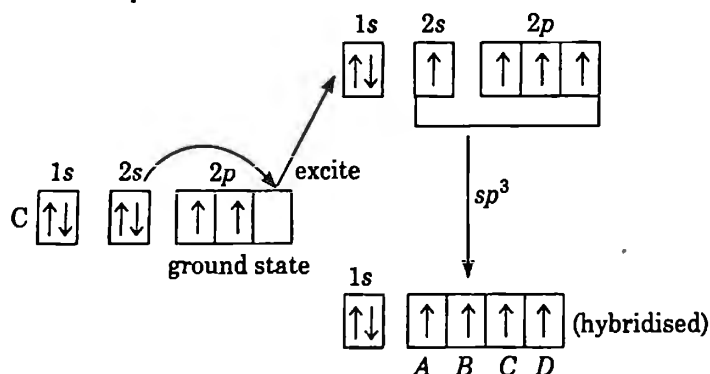
## Applications

(a)  $\text{BeH}_2$ 

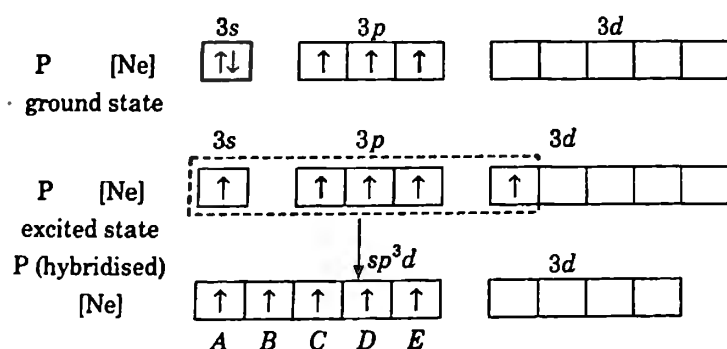
A and B  $sp$ -hybrid orbitals form  $\sigma$  bonds with H by  $(sp-s)$  overlap.

(b)  $\text{BH}_3$ 

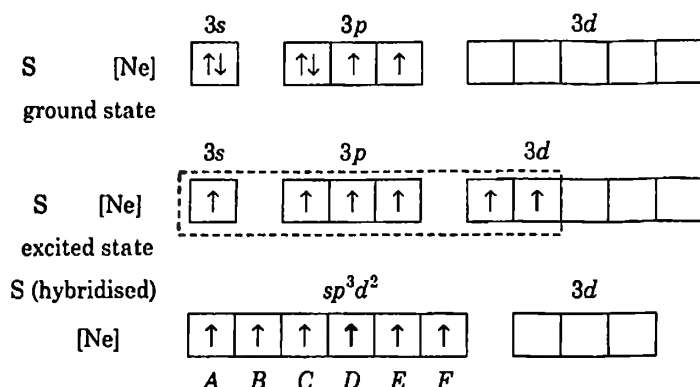
A, B and C  $sp^2$ -hybrid orbitals form  $\sigma$  bonds with H by  $(sp^2-s)$  overlap.

(c)  $\text{CH}_4$ 

A, B, C and D  $sp^3$ -hybrid orbitals form  $\sigma$  bonds with H by  $(sp^3-s)$  overlap.

(d)  $\text{PCl}_5$ 

$sp^3d$  hybrid orbitals form  $\sigma$ -bonds with Cl atoms

(e)  $\text{SF}_6$ 

$sp^3d^2$  hybrid orbitals form  $\sigma$ -bonds with F-atoms

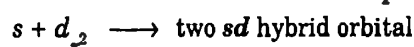
## DEEP Focus

There are also two types of new hybrid orbitals

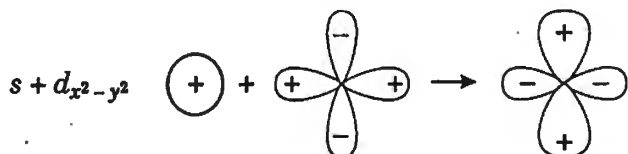
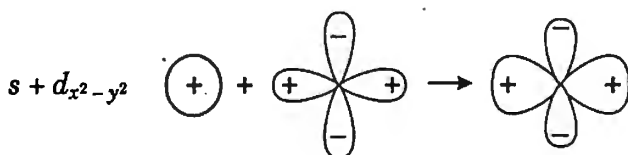
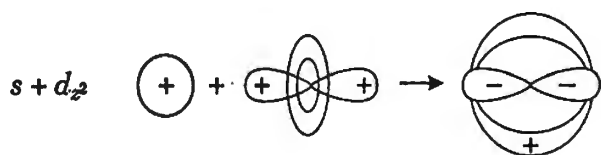
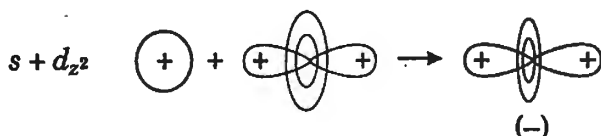
(i) an  $sd$  hybrid orbital

and (ii) an  $pd$  hybrid orbital.

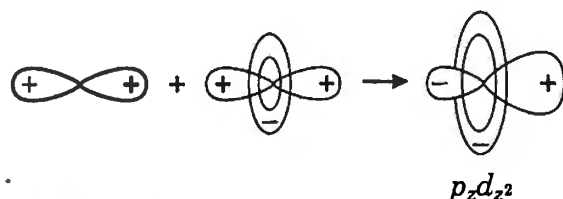
(i) is formed by interaction of one  $s$ - and one  $d_{x^2-y^2}$ -orbital



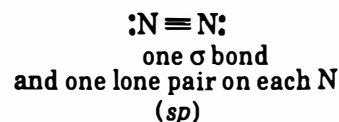
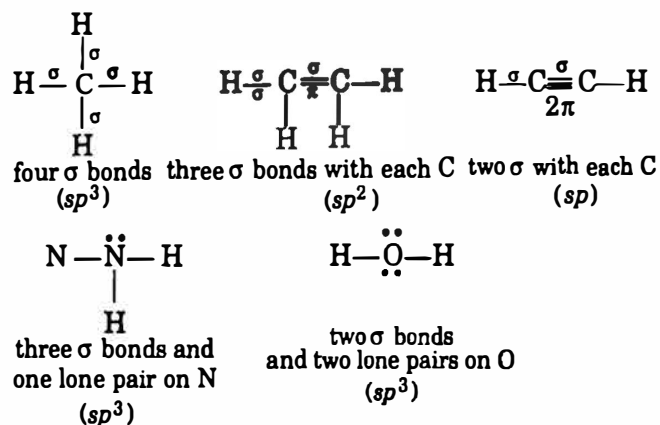
Combination of  $d_{x^2-y^2}$  with  $s$  increases the (+) lobes of  $d_{x^2-y^2}$  and diminishes the negative one. Angular hybrid results from combination of  $s$  with other  $d$ -orbitals.



(ii)  $p_z \pm d_{x^2-y^2} \rightarrow$  Each combination increases one lobe of  $d_{x^2-y^2}$  and diminishes the other.



- While determining type of hybridization on the atom,  $\pi$  bonds are never taken into account, but lone pairs are always considered.



Bond energies and bond lengths of different types of bonds have been summarised in Table 2.9.

Table 2.9 Some Representative Bond Energies and Bond Lengths

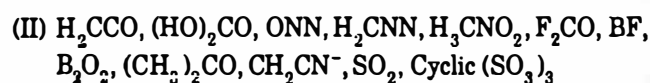
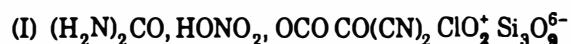
| Bond            | Bond energy<br>kJ mol <sup>-1</sup> | Bond length pm | Bond | Bond energy<br>kJ mol <sup>-1</sup> | Bond length<br>pm | Bond  | Bond energy<br>kJ mol <sup>-1</sup> | Bond<br>length<br>pm |
|-----------------|-------------------------------------|----------------|------|-------------------------------------|-------------------|-------|-------------------------------------|----------------------|
| H—H             | 435                                 | 74             | C=C  | 611                                 | 134               | N—N   | 163                                 | 145                  |
| C—H             | 414                                 |                | C≡C  | 837                                 | 120               | N=N   | 418                                 | 123                  |
| $sp^3$ -H       |                                     | 110            | C—N  | 305                                 | 147               | N≡N   | 946                                 | 109                  |
| $sp^2$ -H       |                                     | 109            | C=N  | 615                                 | 128               | N—O   | 230                                 | 136                  |
| $sp$ -H         |                                     | 108            | C≡N  | 891                                 | 116               | N=O   | 590                                 | 115                  |
| H—N             | 389                                 | 100            | C—O  | 360                                 | 143               | O—O   | 142                                 | 145                  |
| H—O             | 464                                 | 97             | C=O  | 728                                 | 123               | O=O   | 498                                 | 121                  |
| H—S             | 368                                 | 132            | C—Cl | 326                                 | 177               | F—F   | 159                                 | 128                  |
| H—F             | 569                                 | 101            |      |                                     |                   | Cl—Cl | 243                                 | 199                  |
| H—Cl            | 431                                 | 136            |      |                                     |                   | Br—Br | 192                                 | 228                  |
| H—Br            | 368                                 | 151            |      |                                     |                   | I—I   | 151                                 | 266                  |
| H—I             | 297                                 | 170            |      |                                     |                   |       |                                     |                      |
| C—C             | 347                                 |                |      |                                     |                   |       |                                     |                      |
| $sp^3$ - $sp^3$ |                                     | 154            |      |                                     |                   |       |                                     |                      |
| $sp^3$ - $sp^2$ |                                     | 150            |      |                                     |                   |       |                                     |                      |
| $sp^2$ - $sp^2$ |                                     | 147            |      |                                     |                   |       |                                     |                      |
| $sp^3$ - $sp$   |                                     | 146            |      |                                     |                   |       |                                     |                      |
| $sp^2$ - $sp$   |                                     | 143            |      |                                     |                   |       |                                     |                      |
| $sp$ - $sp$     |                                     | 137            |      |                                     |                   |       |                                     |                      |

## Target Practice 2

1. Steric number of the central atom in  $\text{IF}_4^-$  is .....
2. Steric number and predicted geometry of  $\text{AX}_6$  is .....
3. Which of the following in each pair will have the larger bond angle?

| I                               | II    |
|---------------------------------|-------|
| (a) $\text{CH}_4, \text{NH}_3$  | ..... |
| (b) $\text{OF}_2, \text{OCl}_2$ | ..... |
| (c) $\text{NH}_3, \text{NF}_3$  | ..... |
| (d) $\text{PH}_3, \text{NH}_3$  | ..... |

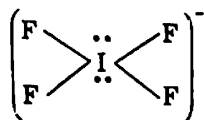
4. Using the general principle of isoelectric groups, identify the species of line (II) that are "isoelectronic" with those of line (I). Each entry might have more than one "isoelectronic" partner in the other line.





## Answers

1. Two lone pairs + four bonding atoms = 6



2. Six, octahedral

3. (a)  $\text{CH}_4$  (b)  $\text{OCl}_2$  (c)  $\text{NH}_3$  (d)  $\text{NH}_3$

4. For each horizontal line shown the molecules, ions, or the groups underlined are "isoelectronic".

| (I)                                  | (II)                                                                                  |
|--------------------------------------|---------------------------------------------------------------------------------------|
| <u>H</u> $\text{ONO}_2$              | <u>CH</u> $_3\text{NO}_2$                                                             |
| ( <u>H</u> ) $_2\text{N}_2\text{CO}$ | ( <u>HO</u> ) $_2\text{CO}$ , <u>F</u> $_2\text{CO}$ , ( <u>CH</u> ) $_3)_2\text{CO}$ |
| ( <u>CN</u> ) $_2$                   | <u>B</u> $_2\text{O}_2$ (2 × 9 electron)                                              |
| <u>ClO</u> $_2^+$                    | <u>SO</u> $_2$ (18 electrons)                                                         |
| <u>Si</u> $_3\text{O}_9^{6-}$        | ( <u>SO</u> ) $_3)_3$ (3 × 40 electrons)                                              |

## Practice Exercise 2

- The H—P—H bond angles in  $\text{PH}_3$  are smaller than the H—N—H angles in  $\text{NH}_3$ . Explain.
- $\text{PCl}_5$  has the shape of a trigonal bipyramid whereas  $\text{IF}_5$  has the shape of square pyramid. Explain.
- Which one of each of the following pairs is expected to have the larger bond angle?
  - $\text{H}_2\text{O}$  and  $\text{NH}_3$
  - $\text{SF}_2$  and  $\text{BeF}_2$
  - $\text{BF}_3$  and  $\text{BF}_4^-$
  - $\text{NH}_3$  and  $\text{NF}_3$
- Which of the following molecules are linear?  
 $\text{ICl}_2$ ,  $\text{IF}_2^+$ ,  $\text{OF}_2$ ,  $\text{SnI}_2$ ,  $\text{CdBr}_2$
- Which molecule out of  $\text{AX}_3$ ,  $\text{AX}_4$ ,  $\text{AX}_5$  and  $\text{AX}_6$ , is most likely to have a trigonal bipyramidal structure? If the central atom, A, has no lone pairs, what type of Hybridization will it have?
- Two of the following species have the same shape. Which are these two? What is their shape? What are the shapes of the other two?  $\text{NI}_3$ ,  $\text{I}_3^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{NO}_3^-$
- Use the VSEPR model to predict the shape of
  - $\text{OSF}_2$
  - $\text{O}_2\text{SF}_2$
  - $\text{XeF}_4$
  - $\text{ClO}_4^-$
  - $\text{I}_3^-$
- Predict the geometrical shapes of the following molecules and then predict which molecules you would expect to have resultant dipole moments: (also refer sec-dipole moment)
  - $\text{SO}_2$
  - $\text{NH}_3$
  - $\text{H}_2\text{S}$
  - $\text{C}_2\text{H}_4$
  - $\text{SF}_6$
  - $\text{CH}_2\text{Cl}_2$
- Match the terms in A with those in B
 

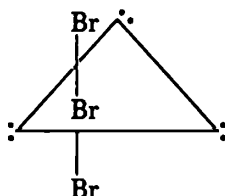
|                            |                       |
|----------------------------|-----------------------|
| (A)                        | (B)                   |
| (a) $\text{NH}_3$ molecule | (i) Heitler London    |
| (b) $\text{SF}_6$          | (ii) $sp^3d^2$        |
| (c) Metallic bond          | (iii) Pyramidal shape |
| (d) VB approach            | (iv) Mobile electrons |
| (e) MO theory              | (v) Bond order        |
| (f) VSEPR theory           | (vi) Bond angles      |
- Two different bond lengths are observed in  $\text{PF}_5$  molecule, but only one bond length is observed in  $\text{SF}_6$ . Explain.
- Draw an electron dot structure for  $\text{Br}_3^-$ . Deduce an approximate value for the bond angle and explain your deduction.
- Predict the shapes of
  - $\text{TeCl}_4$
  - $\text{ClO}_3$
  - $\text{ClO}_2^+$
  - $\text{ClO}_3^+$
- For each horizontal line shown the molecules, ions, or the groups underlined are "isoelectronic".
 

|                                      |                                                                                       |
|--------------------------------------|---------------------------------------------------------------------------------------|
| (I)                                  | (II)                                                                                  |
| <u>H</u> $\text{ONO}_2$              | <u>CH</u> $_3\text{NO}_2$                                                             |
| ( <u>H</u> ) $_2\text{N}_2\text{CO}$ | ( <u>HO</u> ) $_2\text{CO}$ , <u>F</u> $_2\text{CO}$ , ( <u>CH</u> ) $_3)_2\text{CO}$ |
| ( <u>CN</u> ) $_2$                   | <u>B</u> $_2\text{O}_2$ (2 × 9 electron)                                              |
| <u>ClO</u> $_2^+$                    | <u>SO</u> $_2$ (18 electrons)                                                         |
| <u>Si</u> $_3\text{O}_9^{6-}$        | ( <u>SO</u> ) $_3)_3$ (3 × 40 electrons)                                              |
- Match each of the following species with one of these Hybridization schemes
 

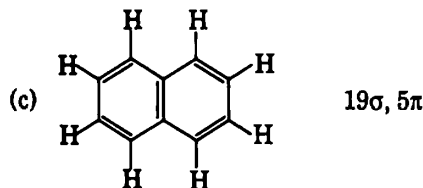
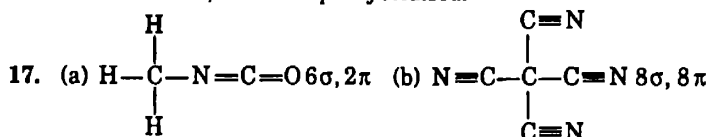
|               |                     |
|---------------|---------------------|
| (I)           | (II)                |
| (A) $sp$      | (a) $\text{SF}_6$   |
| (B) $sp^2$    | (b) $\text{CS}_2$   |
| (C) $sp^3$    | (c) $\text{SnCl}_4$ |
| (D) $sp^3d$   | (d) $\text{NO}_3^-$ |
| (E) $sp^3d^2$ | (e) $\text{AsF}_5$  |
- The ion  $\text{ClF}_2^-$  is linear, but the ion  $\text{ClF}_2^+$  is bent. Describe Hybridization schemes for the central Cl atom to account for this difference in structure.
- $\text{SbF}_3$  reacts with  $\text{XeF}_4$  and  $\text{XeF}_6$  to form ionic compounds  $\text{XeF}_3^+\text{SbF}_6^-$  and  $\text{XeF}_5^+\text{SbF}_6^-$ . Describe the geometries of these two compounds.
- What are the Hybridization states of the C and N atoms in the following molecule?
- What are the total number of  $\sigma$  and  $\pi$  bonds in
  - methyl isocyanate  $\text{CH}_3\text{NCO}$ ?
  - tetracyanomethane  $\text{C}(\text{CN})_4$ ?
  - naphthalene  $\text{C}_{10}\text{H}_8$
- When ethene reacts with  $\text{H}_2$ , ethane is formed. Which bond is affected?
- Although both carbon and silicon are in group IVA (14), very few  $\text{Si}=\text{Si}$  bonds are known. Explain.
- Aspirin has the following connections among atoms. Complete the electron dot structure for aspirin. Also give the  $\sigma$  and  $\pi$  bonds and Hybridization of each atom.

## Answers

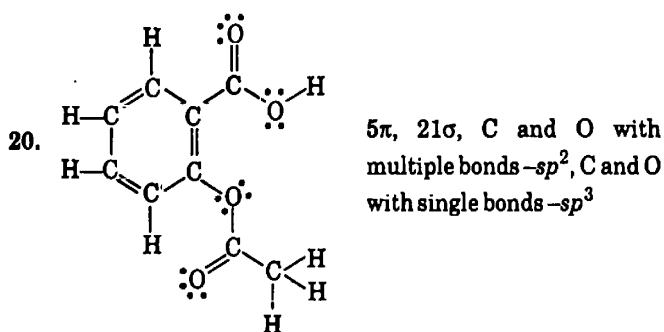
1. See text    2. See text
3. (a)  $\text{NH}_3$  (b)  $\text{BeF}_2$  (c)  $\text{BF}_3$  (d)  $\text{NH}_3$     4.  $\text{ICl}_2$ ,  $\text{CdBr}_2$
5.  $\text{AX}_5$ ,  $sp^3d$
6.  $\text{NI}_3$  and  $\text{SO}_3^{2-}$  are trigonal pyramidal;  $\text{I}_3^-$  is linear;  $\text{NO}_3^-$  is trigonal planar.
7. (a) trigonal pyramidal (b) tetrahedral (c) square planar (d) tetrahedral (e) linear.
8. Resultant dipole moment in (a), (b), (c) and (f).
9. (a)—(iii) (b)—(ii) (c)—(iv) (d)—(i) (e)—(v) (f)—(vi)
10.  $\text{PCl}_5$  has trigonal bipyramidal structure in which bond angles of  $90^\circ$  and  $120^\circ$  exist, hence, two types of bond length, while in case of  $\text{SF}_6$  there is only one type of angle ( $90^\circ$ ) in octahedral structure.
11. The molecule should be linear, using two axial  $dsp^3$  orbital, with three other  $dsp^3$  orbitals occupied by lone pairs.
12. (a) seesaw shaped, (b) trigonal pyramid with bond angles less than  $109.5^\circ$ , (c) angular, with bond angles less than  $109.5^\circ$  (d) trigonal.
13. A—b; B—d; C—c; D—e; E—a
14.  $\text{ClF}_2^-$  —  $sp^3d$  (three lone pairs on Cl at three corners and two F at vertices)  
 $\text{ClF}_2^+$  —  $sp^3$  (two lone pairs on Cl)
15.  $\text{XeF}_3^+$     T-shaped  
 $\text{XeF}_5^+$     Square pyramidal  
 $\text{SbF}_6^-$     Octahedral



16. Each C and N, both are  $sp^2$  hybridised.

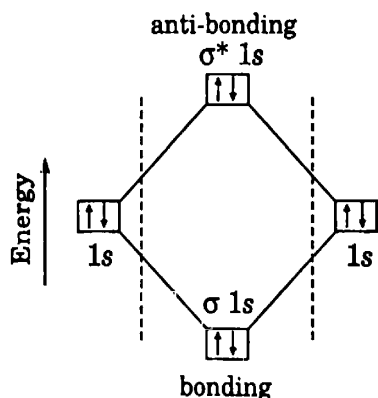


18.  $\pi$ -bond of  $\text{C}=\text{C}$  is affected, thus  $\pi$  bond is more reactive than  $\sigma$ -bond.
19. Larger size of silicon (Si) results in poor sideways overlap of p-orbitals to form  $\pi$ -bond.



## Molecular Orbital Theory

- There is Linear Combination of Atomic Orbitals (LCAO) to form Molecular Orbitals (MOs)
- The number of MO produced is equal to the number of atomic orbitals that are combined.
- Two types of MOs are formed :
  - \* Bonding MO at a lower energy than the original atomic orbital
  - \* Anti-bonding MO at a higher energy

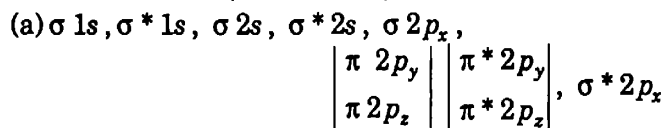


Following MOs are formed when atomic orbitals overlap :

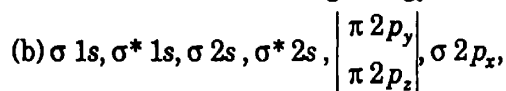
| Atomic orbitals | Molecular orbitals |                 |
|-----------------|--------------------|-----------------|
|                 | Bonding            | Anti-bonding    |
| $1s + 1s$       | $\sigma 1s$        | $\sigma^* 1s$   |
| $2s + 2s$       | $\sigma 2s$        | $\sigma^* 2s$   |
| $2p_x + 2p_x$   | $\sigma 2p_x$      | $\sigma^* 2p_x$ |
| $2p_y + 2p_y$   | $\pi 2p_y$         | $\pi^* 2p_y$    |
| $2p_z + 2p_z$   | $\pi 2p_z$         | $\pi^* 2p_z$    |

( $\sigma$  before MO indicates that bond formed is  $\sigma$  type and  $\pi$  before it indicates bond formed is  $\pi$ . \* indicates anti-bonding MO)

- Electrons are filled in the increasing energy of the MO which is in order (Aufbau rule)



increasing energy (for electrons  $> 14$ )



increasing energy (for electrons  $\leq 14$ )

## DEEP Focus

- $\pi 2p_y, \pi 2p_z$  and also  $\pi^* 2p_y, \pi^* 2p_z$  are degenerate levels (with same energy). Electrons enter MO of identical energies singly before they pair up (Hund's rule).
- The maximum number of electrons that can be assigned to given MO is two (Pauli's exclusion principle).
- Number of bonds between two atoms is called **bond-order** and is given by

$$\text{Bond-order} = \left( \frac{N_B - N_A}{2} \right)$$

where  $N_B$  = number of electrons in bonding MO

$N_A$  = number of electrons in anti-bonding MO

- For a stable molecule/ion,  $N_B > N_A$
- Given molecule or ion is paramagnetic if it has unpaired electrons in MO, otherwise diamagnetic.
- MOs formation for  $H_2$  and  $O_2$  are represented in Figs. 2.4 and 2.5 respectively.

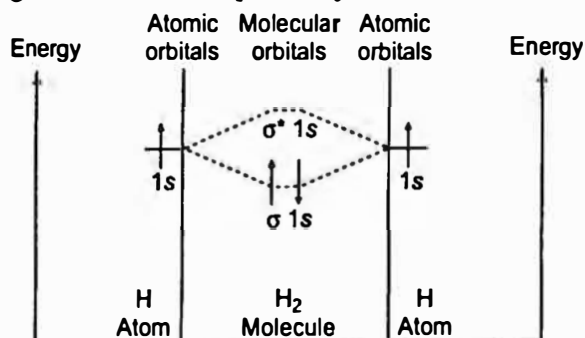


Fig. 2.4 Electronic configuration, atomic and molecular orbitals for hydrogen

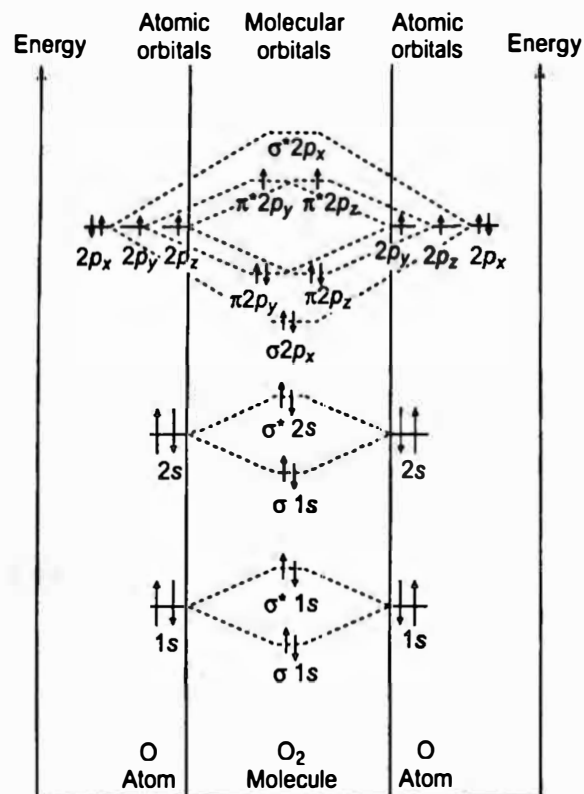


Fig. 2.5 Electronic configuration, atomic and molecular orbitals for oxygen

- Various other species have been summarised in Tables 2.10 and 2.11.

Table 2.10 MO Electronic Configuration of Diatomic Species up to 14 Electrons

| S. no. | Molecule or ion | Total no. of electrons | Electronic configuration |               |                  |               |            |            |               | $N_B$ | $N_A$ | Bond order | Paramagnetic (P) diamagnetic (D) |
|--------|-----------------|------------------------|--------------------------|---------------|------------------|---------------|------------|------------|---------------|-------|-------|------------|----------------------------------|
|        |                 |                        | $\sigma 1s$              | $\sigma^* 1s$ | $\sigma 2s$      | $\sigma^* 2s$ | $\pi 2p_y$ | $\pi 2p_z$ | $\sigma 2p_x$ |       |       |            |                                  |
| 1.     | $H_2$           | 2                      | 2                        |               |                  |               |            |            |               | 2     | 0     | 1.0        | D                                |
| 2.     | $H_2^+$         | 1                      | 1                        |               |                  |               |            |            |               | 1     | 0     | 0.5        | P                                |
| 3.     | $He_2$          | 4                      | 2                        | 2             |                  |               |            |            |               | 2     | 2     | 0.0        | D                                |
| 4.     | $He_2^+$        | 3                      | 2                        | 1             |                  |               |            |            |               | 2     | 1     | 0.5        | P                                |
| 5.     | $Li_2$          | 6                      | 2                        | 2             | 2                |               |            |            |               | 4     | 2     | 1.0        | D                                |
| 6.     | $Be_2$          | 8                      | 2                        | 2             | 2                | 2             |            |            |               | 4     | 4     | 0.0        | D                                |
| 7.     | $B_2$           | 10                     | 2                        | 2             | 2                | 2             | 1          | 1          |               | 6     | 4     | 1.0        | P                                |
| 8.     | $C_2$           | 12                     | 2                        | 2             | 2                | 2             | 2          | 2          |               | 8     | 4     | 2.0        | D                                |
| 9.     | $N_2$           | 14                     | 2                        | 2             | 2                | 2             | 2          | 2          | 2             | 10    | 4     | 3.0        | D                                |
| 10.    | $O_2^{2+}$      | 14                     |                          |               | (same as $N_2$ ) |               |            |            |               | 10    | 4     | 3.0        | D                                |
| 11.    | $N_2^+$         | 13                     | 2                        | 2             | 2                | 2             | 2          | 2          | 1             | 9     | 4     | 2.5        | P                                |
| 12.    | $CN^-$          | 14                     |                          |               | (same as $N_2$ ) |               |            |            |               | 10    | 4     | 3.0        | D                                |

Table 2.11 MO Electronic Configuration of Diatomic Species of More Than 14 Electrons

| S. No. | Molecule or ion              | Total no. of electrons | Electronic configuration |               |             |               |               |            |            |              |              |                 | $N_B$ | $N_A$ | Bond order | Paramagnetic (P)<br>Diamagnetic (D) |
|--------|------------------------------|------------------------|--------------------------|---------------|-------------|---------------|---------------|------------|------------|--------------|--------------|-----------------|-------|-------|------------|-------------------------------------|
|        |                              |                        | $\sigma 1s$              | $\sigma^* 1s$ | $\sigma 2s$ | $\sigma^* 2s$ | $\sigma 2p_x$ | $\pi 2p_y$ | $\pi 2p_z$ | $\pi^* 2p_y$ | $\pi^* 2p_z$ | $\sigma^* 2p_x$ |       |       |            |                                     |
| 1.     | $O_2$                        | 16                     | 2                        | 2             | 2           | 2             | 2             | 2          | 2          | 1            | 1            |                 | 10    | 6     | 2.0        | P                                   |
| 2.     | $O_2^+$                      | 15                     | 2                        | 2             | 2           | 2             | 2             | 2          | 2          | 1            |              |                 | 10    | 5     | 2.5        | P                                   |
| 3.     | NO                           | 15                     | 2                        | 2             | 2           | 2             | 2             | 2          | 2          | 1            |              |                 | 10    | 5     | 2.5        | P                                   |
| 4.     | $O_2^-$<br>(superoxide ion)  | 17                     | 2                        | 2             | 2           | 2             | 2             | 2          | 2          | 2            | 1            |                 | 10    | 7     | 1.5        | P                                   |
| 5.     | $O_2^{2-}$<br>(peroxide ion) | 18                     | 2                        | 2             | 2           | 2             | 2             | 2          | 2          | 2            | 2            |                 | 10    | 8     | 1.0        | D                                   |
| 6.     | $F_2$                        | 18                     | 2                        | 2             | 2           | 2             | 2             | 2          | 2          | 2            | 2            |                 | 10    | 8     | 1.0        | D                                   |
| 7.     | $Ne_2$                       | 20                     | 2                        | 2             | 2           | 2             | 2             | 2          | 2          | 2            | 2            | 2               | 10    | 10    | 0.0        | D                                   |

- MO electronic configuration is written similar to that of atomic orbitals. For example for  $He_2$  (4 electrons) we write

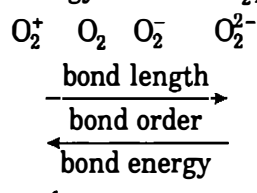
$\sigma 1s^2 \sigma^* 1s^2$  or  $KK^*$  ( $K$  indicates first bonding MO and  $K^*$  anti-bonding MO and are core electrons)

and for  $O_2$  we write

$KK^* \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x^2 \pi 2p_y^2 \pi 2p_z^2 \pi^* 2p_y^1 \pi^* 2p_z^1$

In  $O_2$ ,  $\pi^* 2p_y$  and  $\pi^* 2p_z$  each has one electron being degenerate levels (of equal energy) hence it is paramagnetic.

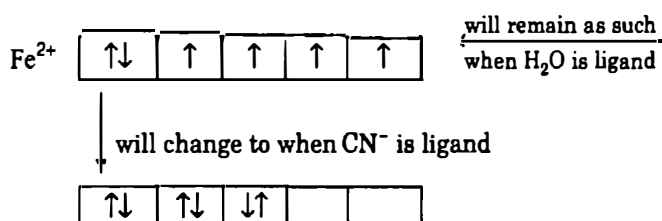
- Greater the bond order, larger the bond length and greater the bond energy. Thus for  $O_2$ ,  $O_2^+$ ,  $O_2^-$ ,  $O_2^{2-}$



## Bonding in Complexes

### Valence Bond Theory

- The metal  $M$  loses requisite number of electrons to form cation. Number of electrons lost corresponds to the **oxidation number** of the metal ion.
- The metal ion makes available a number of empty orbitals equal to its **coordination number** for the formation of coordinate bonds with the ligand orbitals.
- A weak ligand (like  $H_2O$ ) will not affect the electronic configuration of the metal/metal ion.
- A strong ligand (like  $CN^-$ ,  $OH^-$  etc.) will make unpaired electrons paired. (Also refer chapter-18)



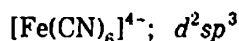
- The metal ion orbitals hybridise to form a new set of equivalent hybridised orbitals with definite stereochemical directions and summarised in Table 2.12.

Table 2.12 Common Type of Hybridization and Geometry of Complexes

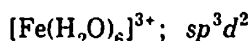
| Coordination number (CN) | Hybridization         | Geometry             | Examples                                                      |
|--------------------------|-----------------------|----------------------|---------------------------------------------------------------|
| 2                        | $sp$                  | Linear               | $[Ag(NH_3)_2]^+$                                              |
| 3                        | $sp^2$                | Trigonal planar      | $[HgI_3]^-$ , $[Cu(PMe_3)_3]^-$                               |
| 4                        | $sp^3$                | Tetrahedral          | $[VO_4]^{3-}$ , $[MnO_4]^-$ , $[NiCl_4]^{2-}$ , $Ni(CO)_4$    |
| 4                        | $dsp^2$               | Square planar        | $[Cu(NH_3)_4]^{2+}$ , $[Ni(CN)_4]^{2-}$ , $[Pt(NH_3)_4]^{2+}$ |
| 5                        | $sp^3d$ , $dsp^3$     | Trigonal bipyramidal | $[CuCl_5]^{3-}$ , $[Ni(CN)_5]^{3-}$ , $[Fe(CO)_5]$            |
| 6                        | $d^2sp^3$ , $sp^3d^2$ | Octahedral           | $[Fe(CN)_6]^{4-}$ , $[Fe(H_2O)_6]^{3+}$                       |

## DEEP Focus

- If there are unpaired electrons the complex ion is said to be **paramagnetic** and magnetic moment is  $= \sqrt{N(N+2)}$  BM where  $N$  is the number of unpaired electrons.
- The complex with so many unpaired electrons is **high spin complex** and that with paired electrons and one or two unpaired electrons is called **low-spin complex**.
- If inner  $d$ -orbital is involved in hybridisation, it is called **inner- $d$  complex** as in



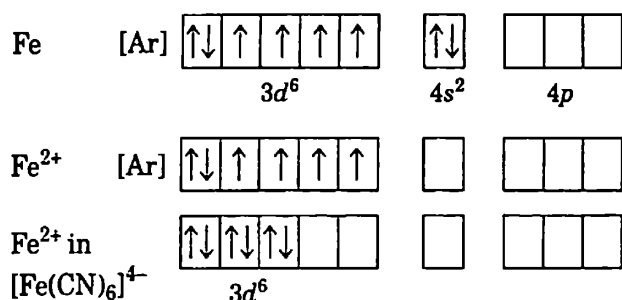
and if outer  $d$ -orbital is involved then it is called **outer- $d$  complex** as in

(i)  $[\text{Fe}(\text{CN})_6]^{4-}$ 

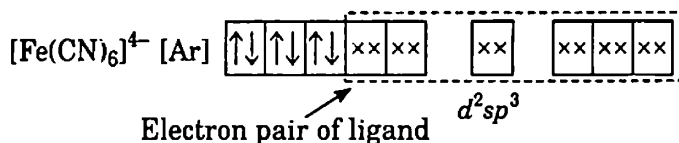
oxidation state of Fe = +2

C.N. of Fe = 6

[in all six empty hybrid orbitals are required by six  $\text{CN}^-$  ligands (a strong ligand)]



( $\text{CN}^-$  is a strong ligand making unpaired electrons paired)

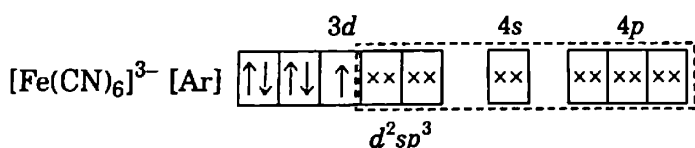


- Complex ion has  $d^2sp^3$  hybridised  $\text{Fe}^{2+}$ .
- Inner- $d$  complex (inner  $d$ -orbital takes part).
- Diamagnetic (since no electron unpaired).
- Magnetic moment = 0 (zero spin complex or spin-paired complex).
- Octahedral geometry, bond angle  $90^\circ$  (Table 7.8).

(ii)  $[\text{Fe}(\text{CN})_6]^{3-}$ 

oxidation number of Fe = +3

If we proceed as in  $[\text{Fe}(\text{CN})_6]^{4-}$  we have



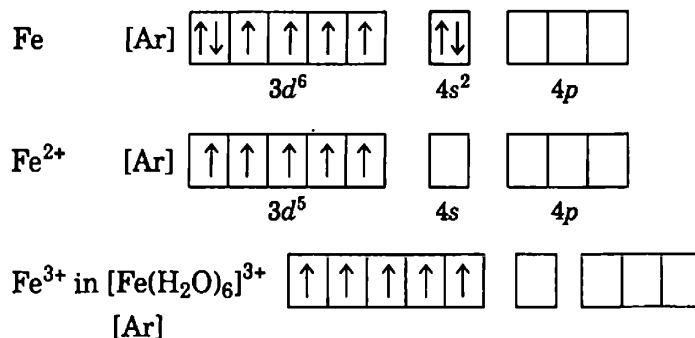
- It has one unpaired electron hence it is paramagnetic with magnetic moment  $\sqrt{3}$  BM.

- All other characteristics remain as in  $[\text{Fe}(\text{CN})_6]^{4-}$ .

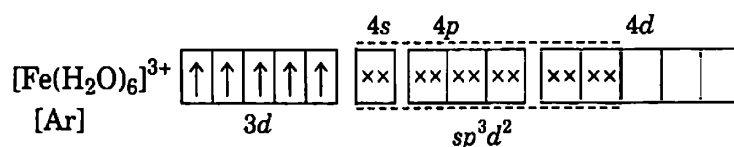
(iii)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ 

oxidation number of Fe = +3

C.N. of Fe = 6



( $\text{H}_2\text{O}$  is a weak ligand hence no change in electron-spin. Outer  $d$ -orbitals will be used for taking electron pairs from  $\text{H}_2\text{O}$ )



- $sp^3d^2$  hybridised Fe
- Outer- $d$  complex,  $\text{H}_2\text{O}$  being a weak ligand does not affect electron spin in  $\text{Fe}^{3+}$ .
- A high spin complex with five unpaired electrons, paramagnetic; magnetic moment is  $\sqrt{35}$  BM.
- Octahedral geometry, bond angle  $90^\circ$ .

(iv)  $[\text{FeF}_6]^{3-}$ 

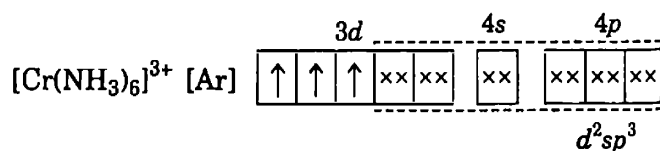
$\text{F}^-$  is a weak ligand like  $\text{H}_2\text{O}$  hence structure is very similar to  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

(v)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ 

oxidation number of Cr = +3

C.N. of Cr = 6

As discussed above

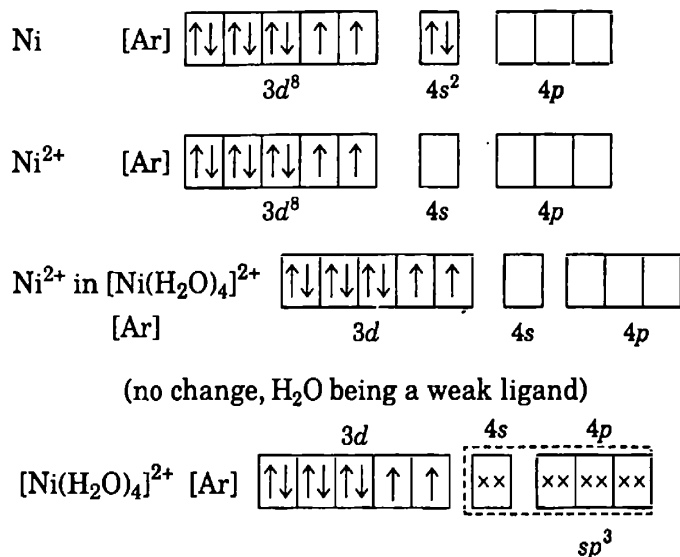


- $d^2sp^3$  hybridised Cr
- Inner- $d$  complex
- Highly paramagnetic, magnetic moment  $\sqrt{15}$  BM.
- Octahedral geometry, bond angle  $90^\circ$ .

(vi)  $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$ 

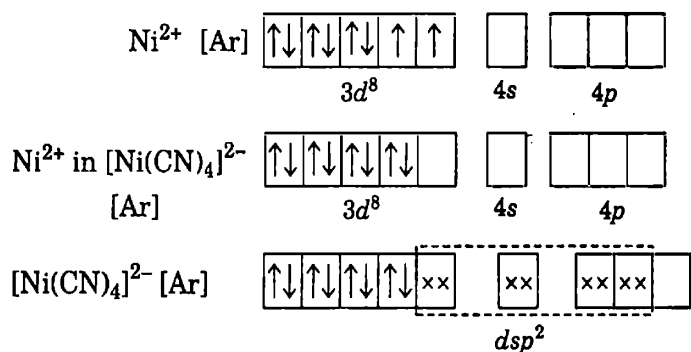
Oxidation number of Ni = +2

CN of Ni = 4



- $sp^3$  hybridised Ni
  - Paramagnetic with two unpaired electrons, magnetic moment is  $2\sqrt{2}$  BM
  - Tetrahedral geometry, bond angle  $109^\circ 28'$
- (vii) [Ni(CN)<sub>4</sub>]<sup>2-</sup>

CN<sup>-</sup> is a strong ligand, hence unpaired electrons in Ni<sup>2+</sup> are paired making one inner  $d$ -orbital vacant for the ligand.

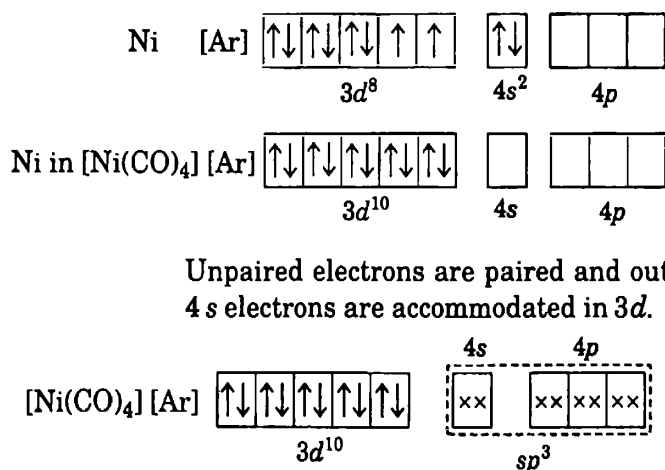


- $dsp^2$  hybridised Ni, inner  $d$ -orbital complex
- Diamagnetic
- Square planar geometry, bond angle  $90^\circ$

(viii) [Ni(CO)<sub>4</sub>] oxidation number of Ni = 0

C.N. of Ni = 4

(CO (carbonyl) is a strong ligand hence electronic configuration is affected)



- $sp^3$  hybridised Ni,
- Diamagnetic,
- Tetrahedral geometry, bond angle  $109^\circ 28'$ .

## Dipole Moment

In H<sub>2</sub>, there is no displacement of the electric charge due to same electronegativity of both H-atoms and the bond is **non-polar**. In HCl, the Cl atom has a more electronegativity than does the H atom. Electronic charge distribution is shifted towards the Cl atom. The H—Cl bond is said to be **polar**.



The magnitude of the charge displacement in a polar covalent bond is measured through a quantity called **dipole moment**  $\mu$ . It is the product of the magnitude of charges ( $\delta$ ) and the distance separating them ( $d$ ). (Here the symbol ( $\delta$ ) suggests a small magnitude of charge, less than the charge on an electron)

$$\mu = \delta \times d$$

- If  $\delta = 4.8 \times 10^{-10}$  esu and  $d = 1 \text{ \AA} = 1 \times 10^{-8} \text{ cm}$  then  $\mu = 4.8 \times 10^{-10} \times 1 \times 10^{-8}$   
 $= 4.8 \times 10^{-18} \text{ esu cm}$

A molecule will have a dipole moment of 1 Debye (1D) if charges of  $1.0 \times 10^{-10}$  esu are separated by a distance of 1  $\text{\AA}$

Thus,  $4.8 \times 10^{-10} \text{ esu cm} = 4.8 \text{ D}$

- In S.I. unit, 1 D =  $3.33 \times 10^{-30}$  coulomb metre (when charge  $\delta = 3.33 \times 10^{-20} \text{ C}$  and  $d = 1 \times 10^{-10} \text{ m}$ ).
- In diatomic molecule,

$$\mu = \delta \times d$$

but in polyatomic molecule with angle  $\theta$ , resultant dipole moment is the vector summation of the vector moments.

$$\begin{array}{c} A \\ \swarrow \quad \searrow \\ B \quad \theta/2 \quad \theta/2 \\ \swarrow \quad \searrow \\ A \end{array} \rightarrow \mu_{\text{resultant}} = 2\mu_{AB} \cos\left(\frac{\theta}{2}\right)$$

where  $\mu_{AB}$  is the vector moment of the side AB.

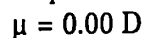
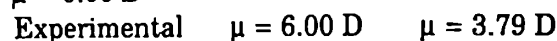
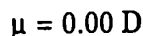
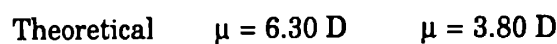
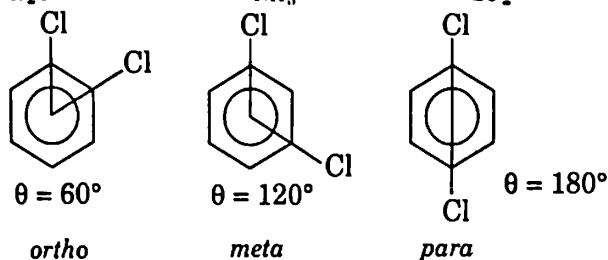
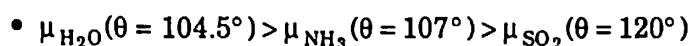
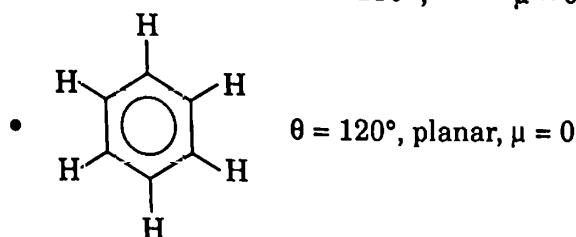
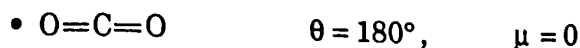
- Also  $\mu_{\text{resultant}} \propto \cos\left(\frac{\theta}{2}\right)$   
 $\propto \frac{1}{\theta}$

Thus, greater the value of  $\theta$ , smaller the value of  $\mu$ .

- Symmetrical molecules without lone pair of electrons will have  $\mu = 0$

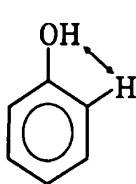


In this case resultant  $\mu_2$  of H—B—H on the left is cancelled by  $\mu_1$  of the right.

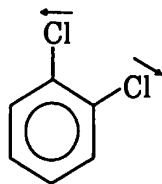


In this case  $\mu$  (*o*-isomer)  $>$   $\mu$  (*m*-isomer)  $>$   $\mu$  (*p*-isomer) but experimental value of *o*-isomer  $<$  theoretical value.

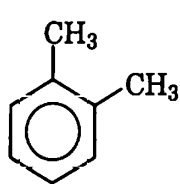
This is due to dipole-dipole repulsion in *o*-isomer that increases bond angle greater than  $60^\circ$  and  $\mu$  decreases.



attraction due to H-bonding  
 $\theta$  decreases,  
 $\mu$  increases



repulsion increases  $\theta$ ,  
 $\mu$  decreases



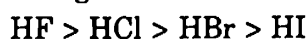
no repulsion or attraction  
no change in actual value.

• % ionic character in a molecule  

$$= \frac{\text{observed value of } \mu}{\text{theoretical value of } \mu} \times 100$$

| Molecule | Dipole moment (Debye) | Bond length (pm) | Per cent ionic character |
|----------|-----------------------|------------------|--------------------------|
| HF       | 1.91                  | 101              | 39.4%                    |
| HCl      | 1.03                  | 136              | 16.0%                    |
| HBr      | 0.78                  | 151              | 10.8%                    |
| HI       | 0.38                  | 170              | 4.7%                     |

Thus, HF is having only approximately 40% ionic character, the order being



- Ionic character can also be decided based on electronegativity difference. Molecule  $\text{H}-\text{X}$  is 50% ionic if electronegativity difference of X and H is 1.7 eV.

Chemists have found that a correlation exists between the difference in electronegativity of bonded atoms and degree of ionicity

(expressed as "% ionic character")

As the difference in electronegativity increases, ionic character increases.

- Based on Pauling's electronegativity scale

$$(\text{EN})_X - (\text{EN})_H = 0.208 \sqrt{\Delta_{\text{H-X}}}$$

where  $\Delta_{\text{H-X}}$  is the extra bond energy in  $\text{kcal mol}^{-1}$  (0.208 is a conversion factor when electronegativities (EN) are given in eV).

$$\Delta_{\text{H-X}} = (\text{actual bond energy (BE) of H-X bond}) - \sqrt{(\text{BE})_{\text{H-H}} (\text{BE})_{\text{X-X}}}$$

- Geometry of the molecule can be decided based on the value of the dipole moment as given in Table 2.13.

Table 2.13 Relation Between Molecular Geometry and Dipole Moment

| Formula       | Molecular geometry                                | Dipole moment                              |
|---------------|---------------------------------------------------|--------------------------------------------|
| $\text{AX}$   | Linear                                            | can be non-zero                            |
| $\text{AX}_2$ | Linear<br>Bent                                    | zero<br>can be non-zero                    |
| $\text{AX}_3$ | Trigonal planar<br>Trigonal pyramidal<br>T-shaped | zero<br>can be non-zero<br>can be non-zero |
| $\text{AX}_4$ | Tetrahedral<br>Square planar<br>See saw           | zero<br>zero<br>can be non-zero            |
| $\text{AX}_5$ | Trigonal bipyramidal<br>Square pyramidal          | zero<br>can be non-zero                    |
| $\text{AX}_6$ | Octahedral                                        | zero                                       |

All X atoms are assumed to be identical.

- Dipole moment of *cis*-geometrical isomer is greater than *trans*-geometrical isomer

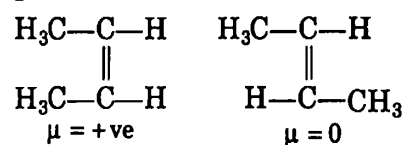
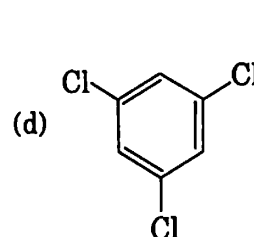
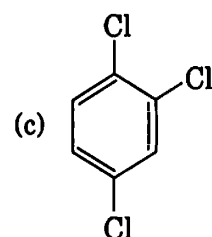
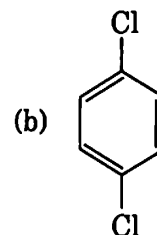
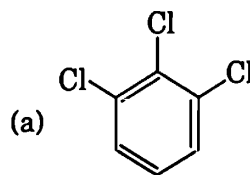


**Illustration 1** Arrange the following compounds in order of increasing dipole moment:



**Solution** (b) and (d) are symmetrical and thus resultant dipole moment is zero.

In (a) bond moments are towards the same direction but in (c) there is net dipole at the  $C_2$  position. Thus, dipole moment of (a) is maximum.

$$(b) = (d) < (c) < (a)$$

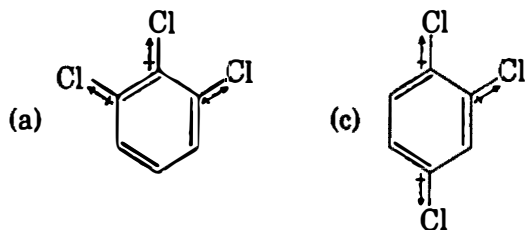
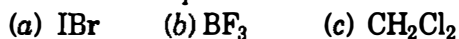


**Illustration 2** Predict whether each of the following molecules has a dipole moment :



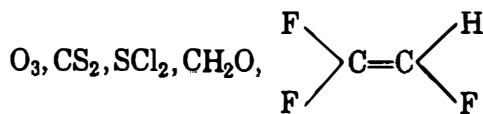
**Solution** (a) Since IBr molecule is diatomic, it has a linear geometry. Bromine is more electronegative than iodine, hence IBr is polar with bromine at the negative end. Thus, the molecule does have a dipole moment.

(b) Since fluorine is more electronegative than boron, each B—F bond in  $BF_3$  is polar and three bond moments are equal. However, the symmetry of a trigonal planar shape means that the three bond moments exactly cancel one another.

(c)  $CH_2Cl_2$  is similar to  $CH_4$  (tetrahedral), but it has three different bond angles : HCH, HCCl, and ClCCl, which are close to but not equal to  $109.5^\circ$ . Since Cl is more electronegative than C and which is more electronegative than H, the bond moments do not cancel and the molecule possesses a dipole moment.  $CH_2Cl_2$  is thus a polar molecule.

Resultant dipole moment is indicated by  $\rightarrow$

**Illustration 3** Predict whether or not the following molecules will have non-zero dipole moments.

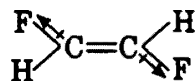


**Solution** In  $O_3$ , all of the atoms are the same, the central oxygen is **hypervalent**, sharing three instead of the usual two electron pairs, and hence is electron-poor and must bear a partial positive charge. VSEPR rules predict a bent molecule, making  $\mu$  **non-zero**.

$\ddot{S}=\ddot{C}=\ddot{S}$ :  $CS_2$ , like  $CO_2$  has zero dipole moment.

$\ddot{Cl}-\ddot{S}-\ddot{Cl}$ :  $SCl_2$ , has two lone pair on S atom, and shows a non-zero  $\mu$  due to noncancelling S—Cl dipoles.

Due to bent structure, it has trigonal planar structure and thus  $\mu \neq 0$



It is the *trans*-isomer. Dipole moments of C—F bonds cancel one each other and thus,  $\mu = 0$ .

## Fajan's Rule

This rule is used to decide relative ionic and covalent character in a molecule. A molecule is predominant covalent if

- smaller the size of cation
- larger the size of anion
- greater the charge on cation and anion
- ion does not have inert gas configuration.

We can also say that these factors favour polarisation.

- Greater the covalent nature

- lower the m.p./b.p.
- larger the lattice energy
- smaller conducting nature
- lower solubility in polar solvent
- higher solubility in non-polar solvent.

(a) LiCl, NaCl, KCl, RbCl, CsCl

Size of cation is the deciding factor (charge of each ion and size of Cl is same)

|                                   |                                       |
|-----------------------------------|---------------------------------------|
| $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ | size of cation                        |
| $\leftarrow$                      | polarisation                          |
| $LiCl > NaCl > KCl > RbCl > CsCl$ | covalent                              |
| $\leftarrow$                      | lattice energy                        |
| $\leftarrow$                      | m.p./b.p.                             |
| $\leftarrow$                      | conductivity                          |
| $\leftarrow$                      | solubility in $H_2O$ (polar solvents) |
| $\leftarrow$                      | solubility in non polar solvent       |

(b) NaF, NaCl, NaBr, NaI

Deciding factor is the size of the anion. Larger size of the anion, greater the polarisation, hence greater the covalent nature.

|                           |                 |
|---------------------------|-----------------|
| $F^- < Cl^- < Br^- < I^-$ | size of anion   |
| $\leftarrow$              | polarisation    |
| $NaF < NaCl < NaBr < NaI$ | covalent nature |
| $\leftarrow$              | lattice energy  |

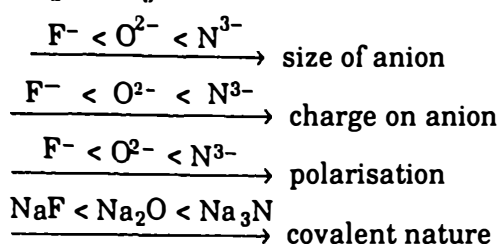
(c) NaCl,  $MgCl_2$ ,  $AlCl_3$ ,  $SiCl_4$ ,  $PCl_5$

|                                               |                  |
|-----------------------------------------------|------------------|
| $Na^+ > Mg^{2+} > Al^{3+} > Si^{4+} > P^{5+}$ | size of cation   |
| $\leftarrow$                                  | max              |
| $\leftarrow$                                  | max              |
| $\leftarrow$                                  | charge on cation |

Greater the charge, smaller the size then greater the polarisation

|                                               |                 |
|-----------------------------------------------|-----------------|
| $Na^+ < Mg^{2+} < Al^{3+} < Si^{4+} < P^{5+}$ | polarisation    |
| $NaCl < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5$     | covalent nature |



(d)  $\text{NaF}$ ,  $\text{Na}_2\text{O}$ ,  $\text{Na}_3\text{N}$ (e)  $\text{CuCl}$  and  $\text{NaCl}$ 

Cations with 18-electron shell have greater polarising power than the 8-electron-shell ions with the same charge and size. This is due to the increased electronegativity of the 18-electron shell ions as the inner electrons have poor shielding effect on the nucleus. Thus,  $\text{CuCl}$  is covalent and  $\text{NaCl}$  is ionic.

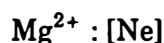
## DEEP Focus

The conditions predicting the nature of bonds are :

| Ionic                                 | Covalent                                        |
|---------------------------------------|-------------------------------------------------|
| 1. Large cation                       | 1. Small cation                                 |
| 2. Small anion                        | 2. Large anion                                  |
| 3. Low charge on cation/or anion      | 3. High charge on cation and/or anion           |
| 4. Cation has noble gas configuration | 4. Cation does not have noble gas configuration |

**Illustration 1** Which of the compounds  $\text{MgCO}_3$  and  $\text{ZnCO}_3$  is thermally more stable? Explain.

**Solution**



$\text{Mg}^{2+}$  has noble-gas electron configuration while  $\text{Zn}^{2+}$  has an 18-electron configuration of the valence-shell. Thus, polarising power of  $\text{Zn}^{2+}$  on an anion is larger than a cation of the same size and charge. Thus, lattice energy of  $\text{ZnCO}_3$  is greater than that of  $\text{MgCO}_3$  and thus,  $\text{ZnCO}_3$  is thermally more stable.

## Hydrogen Bonding

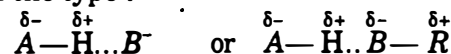
- The concept of the hydrogen bonding was introduced by **Latimer** and **Rodebush** (1920).
- Hydrogen bonding is said to be formed when slightly acidic hydrogen attached to a strongly electronegative atom such as F, N and O, is held with weak electrostatic forces by the non-bonded pair of electrons of another atom. The coordination number of hydrogen in such cases is two. It acts as a bridge between two atoms, to one of which it is covalently bonded, and to the other attached through electrostatic forces, also called **Hydrogen Bond**.

## DEEP Focus

- Of all the electronegative donor atoms, only F, N and O atoms enter into stable hydrogen bond formation.
- The weak electrostatic interaction leading to the hydrogen bond formation is shown by dotted (....) lines. Thus  $X\text{—H} \cdots Y$  represents hydrogen bonding between hydrogen and Y atom.

## Nature of Hydrogen-Bonding

Since the hydrogen bond is formed by the most electronegative elements only, it is considered that its nature is dipole-ion, dipole-induced dipole or dipole-dipole interaction of the type :



(R is the part of the molecule  $\text{B—R}$ )

Bond energy of H—bonding in  $(\overset{\delta+}{\text{H}} \cdots \overset{\delta-}{\text{F}}\text{—}\overset{\delta+}{\text{H}})$  is  $113.4 \text{ kJ mol}^{-1}$  due to dipole-dipole interactions.

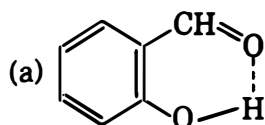
- Energies of H—bonds formed by neutral molecules have been summarised in Table 2.14.

Table 2.14 Energies of Hydrogen Bonds Formed by Neutral Molecules

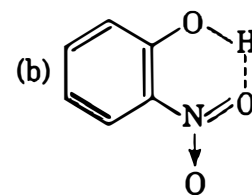
| Bond                         | Energy of the bond is $\text{kJ mol}^{-1}$ |
|------------------------------|--------------------------------------------|
| $\text{F—H} \cdots \text{O}$ | 45                                         |
| $\text{F—H} \cdots \text{F}$ | 23 – 25                                    |
| $\text{O—H} \cdots \text{O}$ | 20 – 30                                    |
| $\text{O—H} \cdots \text{S}$ | 15 – 20                                    |
| $\text{O—H} \cdots \text{F}$ | 12 – 15                                    |
| $\text{N—H} \cdots \text{N}$ | 12 – 25                                    |
| $\text{N—H} \cdots \text{O}$ | 25                                         |

## Intramolecular H-Bonding

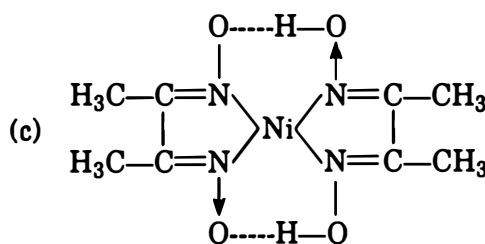
This type of H-bonding occurs when polar H and electronegative atom are present in the same molecule.



*o*-hydroxy benzaldehyde



*o*-nitro phenol

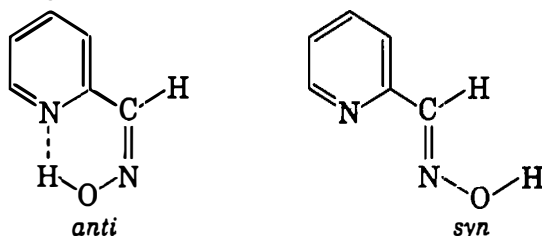


nickel dimethyl glyoximate (a chelate)

The necessary conditions for the formation of intramolecular hydrogen-bonding are :

- the ring formed as a result of hydrogen bonding should be planar.
- a 5- or 6- membered ring should be formed.
- interacting atoms should be placed in such a way that there is minimum strain during the ring closure.

In case of *anti*-form of pyridine-2-carboxaldoxime there is intramolecular hydrogen bonding but it is not shown in *syn*-form

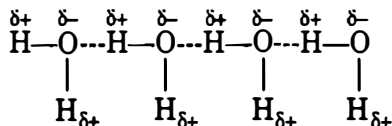


## Intermolecular H-Bonding

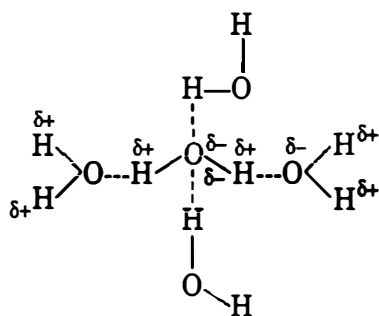
This type of H-bonding takes place between H and electronegative element present in the different molecules of the same substance (as in between  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}$ ) or different substances (as in between  $\text{H}_2\text{O}$  and  $\text{NH}_3$ )

### (a) In water molecules

Due to polar nature of  $\text{H}_2\text{O}$ , there is association of water molecules giving a liquid state of abnormally high boiling point.



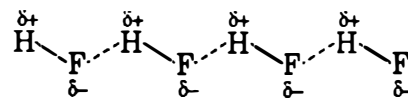
If we actually observe, one water molecule is joined to four water molecules — two with H-atoms and other two with O-atoms. Thus coordination number of water molecule in water is **four**.



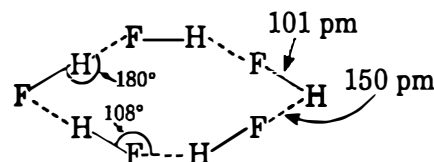
### DEEP Focus

- When ice is formed from liquid water, some air gap is formed (in tetrahedral packing of water molecules). **Due to this volume of ice is greater than liquid water and thus ice is lighter than water.** We can say that density decreases when ice is formed. Reversely when ice melts, density increases but only up to  $4^\circ\text{C}$ , after this intermolecular H-bonding between water molecules breaks hence volume increases and hence density decreases. **Thus, water has maximum density at  $4^\circ\text{C}$ .**

(b) In hydrofluoric acid (HF), there is again association by H-bonding.

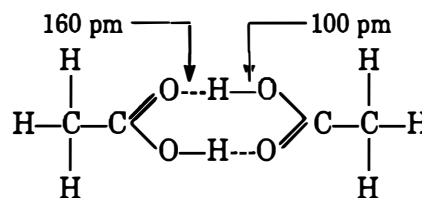


However in the gaseous state, several polymeric forms of the HF molecules exist in which the monomers are held together through H-bonding. A pentagonal arrangement of H—F molecules is shown below :

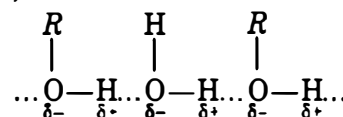


(c) There is also similar H-bonding in alcohol ( $\text{R}-\text{OH}$ ) ammonia ( $\text{NH}_3$ ) and phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) molecules.

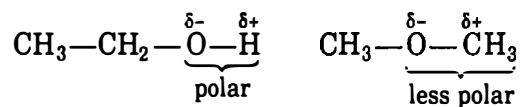
(d) Carboxylic acid dimerises in gaseous state due to H-bonding



(e) Alcohol is said to be highly soluble in water due to *crossed* intermolecular H-bonding (between  $\text{H}_2\text{O}$  and  $\text{R}-\text{OH}$  molecules).

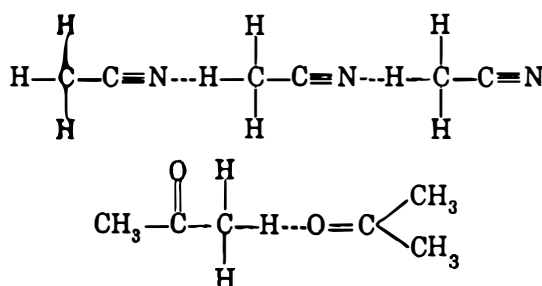


However isomeric ether is less soluble in water due to its (ether) non-polar nature.



### DEEP Focus

(f) Though the hydrogen atoms in a methyl groups are not polarised, if an electronegative group like chloro, carbonyl, nitro or cyano is attached to it, the C—H bond gets polarised due to the inductive effect and the hydrogen atom becomes slightly acidic resulting in the formation of weak hydrogen bonds.



## Consequences of the Hydrogen-Bonding

(a) Due to H-bonding boiling points of water, ammonia, hydrofluoric acid are abnormally high (Fig. 2.6.)

(b) B.P. :  $\text{H}_2\text{O} > \text{HF} > \text{NH}_3 > \text{CH}_4$

M.P. :  $\text{H}_2\text{O} > \text{NH}_3 > \text{HF} > \text{CH}_4$

(c) Solubility of the organic compounds in water is due to H-bond formation.

(d) Due to hydrogen-bonding, viscosity ( $\eta$ ) of the liquid increases as given below (in centipoise (CP)).

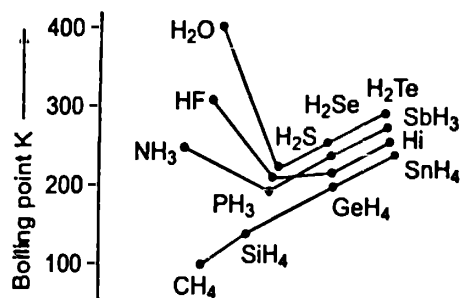
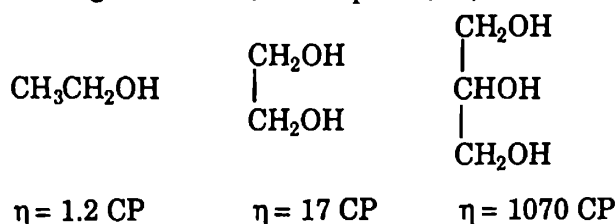
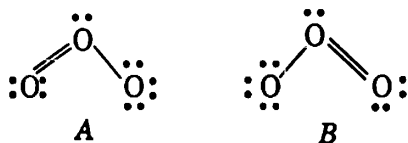


Fig. 2.6

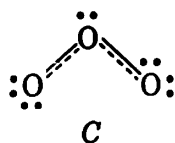
## Resonance

We can write two electronic structures of ozone,  $\text{O}_3$ .



In A, the oxygen—oxygen bond on the left is a double bond and the oxygen—oxygen bond on the right is a single bond. In B, the situation is just the opposite. Experiment shows, however, that the two bonds are identical. Therefore, neither structure A nor B can be correct.

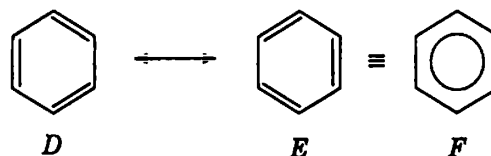
- One of the bonding pairs in ozone is spread over the region of all three atoms rather than associated with a particular oxygen—oxygen bond. This is called **delocalised-bonding**—a type of bonding in which a bonding pair of electrons is spread over a number of atoms rather than localised between two.



- Structures A and B are called **resonating** or **canonical structures** and C is the **resonance hybrid** of these two structures. This phenomenon is called **resonance**: a situation in which more than one plausible structure can be written for a

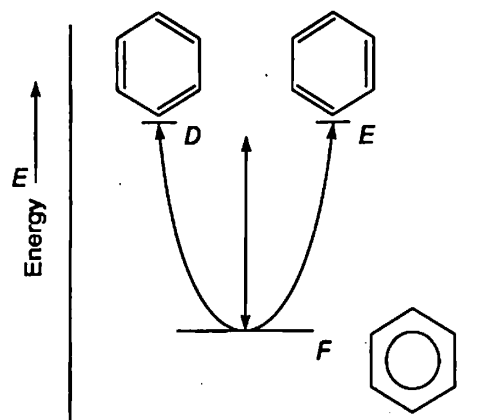
species, and in which the true structure cannot be written at all.

- $\text{O}=\text{O}$  bond length is 121 pm and  $\text{O}-\text{O}$  bond length is 145 pm but in ozone experimental measured  $\text{O}-\text{O}$  bond length is 128 pm suggesting that resonance hybrid is a true representation.
- In benzene, D and E are extreme resonating structure, while F is a resonance hybrid of these two structures,

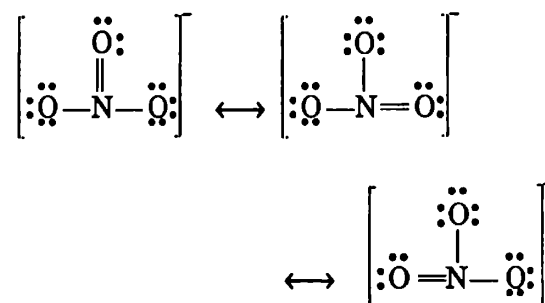


and again carbon—carbon bond length is 140 pm which is intermediate of  $\text{C}-\text{C}$  (154 pm) and  $\text{C}=\text{C}$  (134 pm).

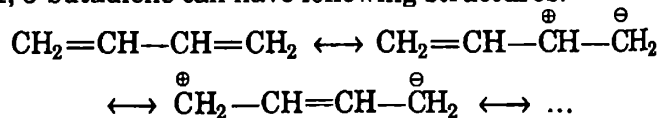
- Difference in the energies of the canonical forms and resonance hybrid form is called **resonance stabilisation energy** ( $\Delta E$ ), and provides stability to the molecule.



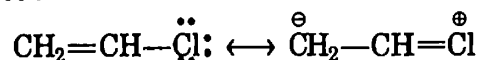
- In nitrate ion, nitrogen—oxygen bond lengths are equal due to resonance,



- 1, 3-butadiene can have following structures:

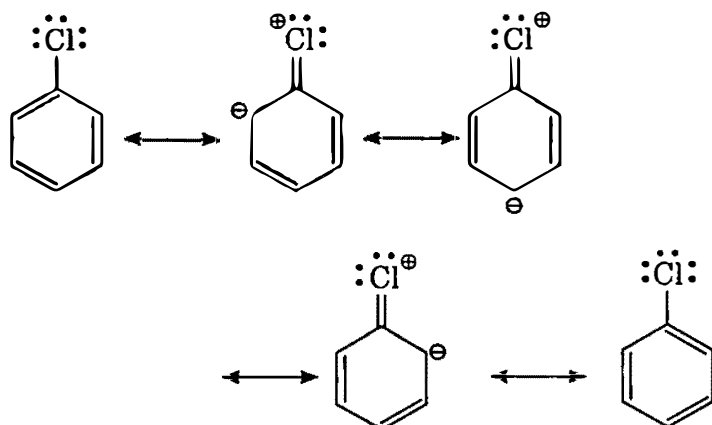


- Vinyl chloride also has following resonating structures:



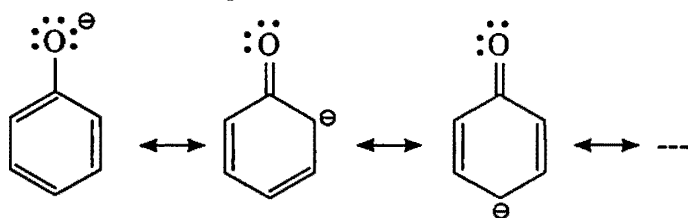
and  $\text{C}-\text{Cl}$  bond is stable.

- C—Cl bond in chlorobenzene is stable due to resonance.

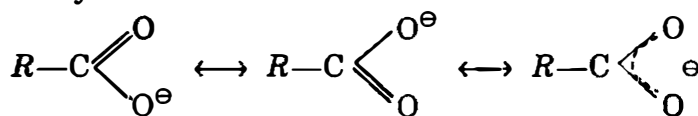


Vinyl chloride and chlorobenzene do not give  $S_N$  reactions due to resonance stabilisation of C—Cl bond.

- Phenoxide ( $C_6H_5O^-$ ) ion is stable due to resonance.

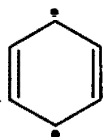


- Thus phenol (which is also an oxo-acid) is more acidic than an alcohol because of resonance charge delocalisation of the phenoxide ion.
- Carbon-oxygen bond lengths in carboxylate ion are equal due to resonance, and thus stability of the carboxylate ion is increased.

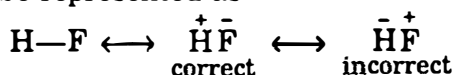


## Conditions for Resonance

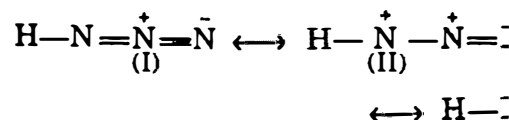
- The canonical forms should not differ in the atomic arrangements. Only positions of the electrons can change. Different canonical forms are separated by  $\longleftrightarrow$  (double headed arrow)
- The number of unpaired electrons should be the same in all the canonical forms. Thus, following structure of benzene is incorrect:



- The positive charge should reside as far as possible, on the less electronegative element and *vice-versa*. Thus, H—F can be represented as

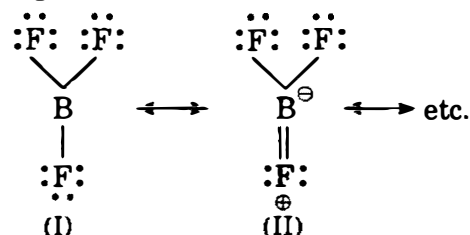


- Like charges should not reside on adjacent atoms. For  $HN_3$ , the structure (II) becomes unstable because of the positive charges on the adjacent nitrogen atoms.



- The larger the number of the contributing structures, the greater the stability of the molecule.
- Greater numbers of the covalent bonds and the stability of the canonical forms.

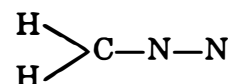
In  $BF_3$ , the actual bond order of B—F bond is more than 1 and is found to have 54%  $\pi$  character. The following resonating structures can be written as:



Thus, (II) is significant due to the addition of a  $\pi$  bond formed.

**Illustration 1** Draw two resonance structures of diazomethane ( $CH_2N_2$ ). Show formal charges.

**Solution** The skeletal structure of  $CH_2N_2$  is,



Two resonance structures are:

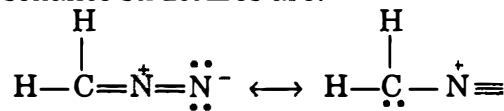
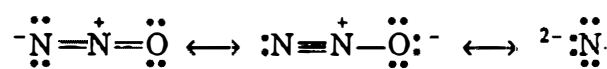


**Illustration 2** Draw three resonance structures of the molecule  $N_2O$  in which the atoms are arranged in NNO. Also indicate formal charges.

**Solution** Resonance structures are shown below:



## Metallic Bonding

- Most metals crystallise in close-packed structures. The ability of metals to conduct electricity must result from strong electronic interactions between 8 to 12 nearest neighbours (which is a coordination number). Bonding in metals is called **metallic bonding**. It results from the attractions among positively charged metal ions and mobile, delocalised electrons belonging to the whole.
- Two models are considered to explain metallic bonding:
  - (a) Band model
  - (b) Electron-sea model

## Band Model

- The interaction of two atomic orbitals, say the 3s-orbitals of two sodium atoms, produces two molecular orbitals, one bonding orbital and one anti-bonding orbital. If  $N$  atomic orbitals interact,  $N$  molecular orbitals are formed. Atoms interact more strongly with nearby atoms than with those farther away. The energy that separates bonding and anti-bonding molecular orbitals resulting from two given atomic orbitals decreases as the interaction (overlap) between the atomic orbitals decreases. When we consider all the possible interactions among one mole of Na atoms, there is formation of series of very closely spaced molecular orbitals (formally) ( $3\sigma$  and  $3\sigma^*s$ ). This consists of a nearly continuous **band** of orbitals belonging to the crystal as a whole. One mole of Na atoms contributes one mole ( $6.02 \times 10^{23}$ ) of valence electrons (Fig. 2.7) thus,  $6.02 \times 10^{23}$  orbitals in the band are half-filled.

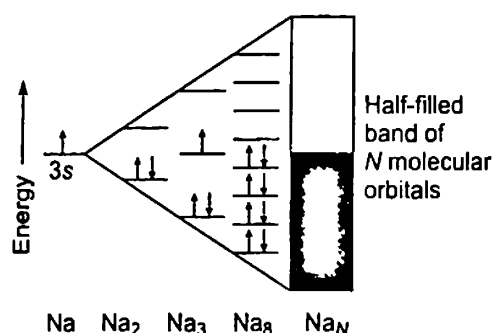


Fig. 2.7 The band of orbitals resulting from interaction of the 3s-orbitals in a crystal of sodium

- The empty 3p atomic orbitals of Na atoms also interact to form a wide band of  $3 \times 6.02 \times 10^{23}$  orbitals. The 3s and 3p atomic orbitals are quite close in energy, so that these bands of molecular orbitals overlap (Fig. 2.8). The two overlapping bands contain  $4 \times 6.02 \times 10^{23}$  orbitals and only  $6.023 \times 10^{23}$  electrons. Because each orbital can hold two electrons, the resulting combination of bands is only one-eighth full.

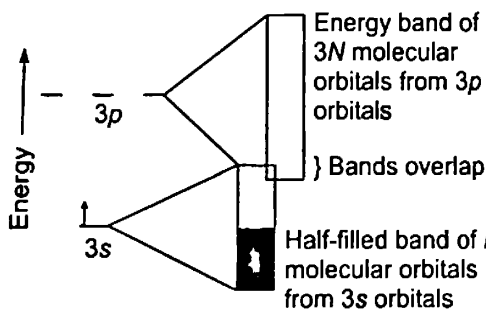


Fig. 2.8 Overlapping of a half-filled "3s" band with an empty "3p" band of  $\text{Na}_N$  crystal

- According to band theory, the highest-energy electrons of metallic crystals occupy either a partially filled band or a filled band that overlaps an empty band. A band within which (or into which) electrons must move to allow electrical conduction is called a **conduction band**. The electrical conductivity of a

metal decreases as temperature increases. The increase in temperature causes thermal agitation of the metal ions. This impedes the flow of electrons when an electric field is applied.

- Crystalline non-metals, such as diamond and phosphorus, are **insulators**—they do not conduct electricity. It is due to the fact that their highest-energy electrons occupy filled bands of molecular orbitals that are separated from the lowest empty band (conduction band) by an energy difference called the **band gap**. In an **insulator**, this band gap is an energy difference that is too large for electrons to jump to get to the conduction band. (Fig. 2.9).

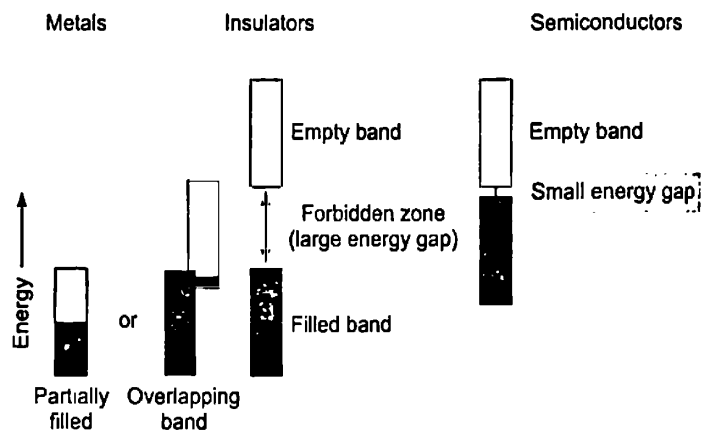


Fig. 2.9 Distinction among metals, insulators and semiconductors. In each case an unshaded area represents a conduction band.

- Elements that are **semiconductors** have filled bands that are only slightly below, but do not overlap with empty bands. They do not conduct electricity at low temperatures, but a small increase in temperature is sufficient to excite some of the highest-energy electrons into the empty conduction band.

## Electron-Sea Model

Metals have

- ability to conduct electricity
- ability to conduct heat
- ease of deformation [that is, the ability to be flattened into sheets (malleability) and to be drawn into wires (ductility)]
- lustrous appearance

One over simplified model that can account for some of these properties is the electron-sea model. The metal is pictured (Fig. 2.10) as a network of positive ions immersed in a "sea of electrons". In lithium, the ions would be  $\text{Li}^+$  and one electron per atom would be contributed to the sea. These free electrons account for the characteristic metallic properties. If the ends of a bar of metal are connected to a source of electric current, electrons from the external source enter the bar at one end. Free electrons pass through the metal and leave the other end at the same rate.

In thermal conductivity no electrons leave or enter the metal, but those in the region being heated gain kinetic energy and transfer this to other electrons.

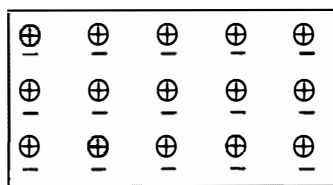


Fig. 2.10 Metallic Bonding in electron-sea model

According to the electron-sea model, the case of deformation of metals can be thought of in this way: If one layer of metal ions is forced across another,

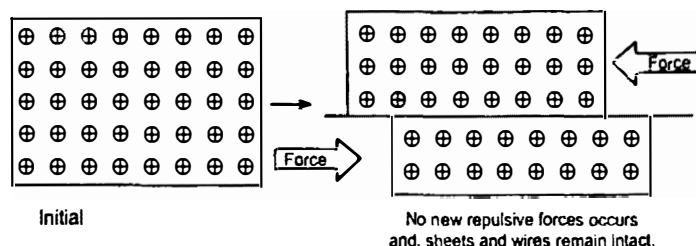
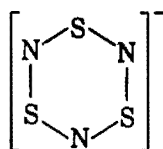


Fig. 2.11 Effect of distortion (by hammering) on metal sheet (assuming electron-sea model)

## Target Practice 3

1. The molecular ion  $S_3N_3^-$  has the cyclic structure



All (S—N) bonds are equivalent

Give at least two equivalent resonance structures

.....  
I                      II

2. For each of the following bond pairs, decide which is the more polar and indicate the negative and positive poles

(a) B—F and B—Cl .....

(b) Si—O and P—P .....

3. What is per cent ionic character in the molecule ( $M—X$ ) if electronegativity difference is 1.7 eV? .....

4. Arrange the following in increasing values of dipole moment (i) HF, HCl, HBr, HI and  $H_2$  .....

(ii)  $H_2O$ ,  $H_2S$ ,  $SO_2$ ,  $CO_2$

5. Select the species with zero dipole moment and maximum dipole moment.

$CH_4$ ,  $CH_3Cl$ ,  $CH_2Cl_2$ ,  $CHCl_3$ ,  $CCl_4$

## Answers

3. 50%

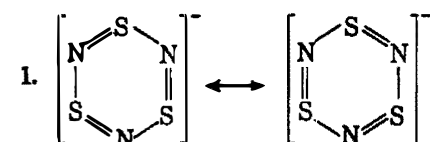
4. (i)  $H_2 < HI < HBr < HCl < HF$

(ii)  $CO_2 < H_2S < SO_2 < H_2O$

5. Zero :  $CCl_4$ ,  $CH_4$

Maximum :  $CH_3Cl$

Order being :  $CH_4 = CCl_4 < CHCl_3 < CH_2Cl_2 < CH_3Cl$



2. (a) B—F > B—Cl  $\overset{\delta+}{B}-\overset{\delta-}{F}$

(b) Si—O > P—P (non-polar)  $\overset{\delta+}{Si}-\overset{\delta-}{O}$

## Practice Exercise 3

1. Which of the following is paramagnetic?

(a)  $O_2^{2-}$  (b)  $O_2^-$   
(c) BN

2.  $N_2$  has a greater dissociation energy than  $N_2^+$ , whereas  $O_2$  has a lower dissociation energy than  $O_2^+$ . Explain.

3. What are the bond-order in each of:  
(a)  $CN^+$  (b) CN  
(c)  $CN^-$ ?

Which of these species should have the shortest bond length?

4. For each of the following species :  $H_2^+$ ,  $C_2^+$  and  $F_2^+$

(a) write the molecular orbital diagram  
(b) determine the bond order

(c) indicate whether the species is paramagnetic or diamagnetic.

5. Arrange the following species in order of increasing stability:  $Li_2$ ,  $Li_2^+$ ,  $Li_2^-$   
Justify your answer using M.O. theory.

6. Explain :

(a)  $[Fe(H_2O)_6]^{2+}$  has magnetic moment ( $\mu$ ) of 4.90 BM, but  $[Fe(CN)_6]^{4-}$  has  $\mu = 0$ .

(b)  $[Co(CN)_6]^{3-}$  is stable but  $[Co(CN)_6]^{4-}$  is unstable.

(c)  $[NiCl_4]^{2-}$  is paramagnetic but  $[Ni(CN)_4]^{2-}$  is diamagnetic.

(d)  $[Co(NH_3)_6]^{3+}$  is diamagnetic but  $[CoF_6]^{3-}$  is paramagnetic.

7. Classify weak and strong ligands out of :  
 (a)  $\text{OH}^-$  (b)  $\text{F}^-$   
 (c)  $\text{I}^-$  (d)  $\text{NH}_3$   
 (e)  $\text{CH}_3\text{COO}^-$  (f)  $\text{en}$   
 (g)  $\text{CN}^-$  (h)  $\text{Cl}^-$   
 (i)  $\text{H}_2\text{O}$
8.  $\text{NH}_3(aq)$  reacts very easily with  $\text{Cu}^{2+}$ ; if acid is added into aqueous solution of  $\text{NH}_3$ , there is no reaction. Explain.
9. Match list I (Complex ions) with list II (number of unpaired electrons) and select the correct answers:

| List I |                                 | List II |      |
|--------|---------------------------------|---------|------|
| A      | $[\text{CrF}_6]^{4-}$           | 1       | one  |
| B      | $[\text{MnF}_6]^{4-}$           | 2       | two  |
| C      | $[\text{Fe}(\text{CN})_6]^{4-}$ | 3       | zero |
| D      | $[\text{Mn}(\text{CN})_6]^{4-}$ | 4       | four |
|        |                                 | 5       | five |

- | A     | B | C | D |
|-------|---|---|---|
| (a) 4 | 1 | 2 | 5 |
| (b) 2 | 5 | 3 | 1 |
| (c) 4 | 5 | 3 | 1 |
| (d) 2 | 1 | 3 | 5 |
10. Select the species which is best described by the statement to the right :  
 (a)  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{CO}$  has a zero dipole moment.  
 (b)  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{HF}$  has highest boiling point.  
 (c)  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$  has the lowest boiling point.  
 (d)  $\text{HOI}$ ,  $\text{HOBr}$ ,  $\text{HOCl}$  is the weakest acid.
11. Which of these molecules would you expect to be polar and which are to be non-polar?  
 $\text{Cl}_2$ ,  $\text{ICl}$ ,  $\text{BF}_3$ ,  $\text{NO}$ ,  $\text{SO}_2$ ,  $\text{XeF}_4$ ,  $\text{H}_2\text{CCl}_2$ ,  $\text{OCS}$ .
12. Calculate the dipole moment of  $\text{HCl}$  molecule if the bond length is 1.2476 Å.
13. If the observed dipole moment of  $\text{LiF}$  is 6.32 D, calculate percentage ionic character; given  $\text{Li}-\text{F}$  bond length is 0.156 nm.
14. Does the molecule  $\text{OCS}$  have a higher or lower dipole moment than  $\text{CS}_2$ .
15. Which has larger lattice energy in :  
 (I)  $\text{Al}_2\text{O}_3$  or  $\text{Al}_2\text{Se}_3$  (II)  $\text{ZnO}$  or  $\text{NaCl}$
16. Aqueous solution of a mixture contains  $\text{LiCl}$ ,  $\text{NaCl}$  and  $\text{KCl}$ . How is  $\text{LiCl}$  separated?
17. Arrange the following in increasing solubility in  $\text{H}_2\text{O}$  :  
 (a)  $\text{NaF}$ ,  $\text{MgO}$ ,  $\text{AlN}$   
 (b)  $\text{MgF}_2$ ,  $\text{CaF}_2$ ,  $\text{AgF}$   
 (c)  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{AgF}$

18. Which of the ion  $\text{Ca}^{2+}$  or  $\text{Cd}^{2+}$  has a stronger polarising action on anions?
19. In going from  $\text{CsF}$  to  $\text{CsI}$ , the melting point of the crystal decreases. Explain.
20. Which one in each of the following pairs is expected to exhibit hydrogen-bonding?  
 (a)  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{OCH}_3$   
 (b)  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{SH}$   
 (c)  $\text{CH}_3\text{OH}$  and  $(\text{CH}_3)_3\text{N}$
21. Which is expected to have the highest melting point?  
 $\text{PH}_3$ ,  $\text{NH}_3$ ,  $(\text{CH}_3)_3\text{N}$
22. Explain:  
 (a) Maleate acid ion is more stable than fumarate acid ion.  
 (b) Dipole moment of o-chlorophenol is less than o-fluorophenol.
23. In each of the following pairs, select the species having the greater resonance stabilisation :  
 (a)  $\text{HNO}_3$  and  $\text{NO}_3^-$   
 (b)  $\text{H}-\text{C}(=\text{O})-\text{H}$  and  $\text{H}-\text{C}(=\text{O})-\text{O}^-$   
 (c)  $\text{H}_2\text{CO}_3$  and  $\text{CO}_3^{2-}$
24. Draw all possible octet structural formulae for  $\text{N}_3^-$ .
25. The structure of 1,3-butadiene is often written as  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ . The distance between the central carbon atoms is 1.46 Å. Comment on the adequacy of the assigned structure.
26. Carbon suboxide has the formula  $\text{C}_3\text{O}_2$ .  $\text{C}-\text{C}$  distances are found to be 130 pm and  $\text{C}-\text{O}$  distances are 120 pm. Write various Lewis structures.
27. How many energy levels are present in the 3s conduction band of a single crystal of sodium weighing 26.8 mg? How many electrons are present in this band?
28. Which of the following factors are especially important in determining whether an element has metallic properties?  
 (a) Atomic number  
 (b) Atomic weight  
 (c) Number of valence electrons  
 (d) Number of vacant atomic orbitals  
 (e) Total number of electronic shells in the atom.
29. What is the energy gap in band theory? Compare its size in conductors, semiconductors and insulators.
30. Compare the temperature dependence of electrical conductivity of a metal with that of a typical metalloid.
31. What single factor accounts for the ability of metals to conduct both heat and electricity in the solid state? Why are ionic solids poor conductors of heat and electricity even though they are composed of charged particles?

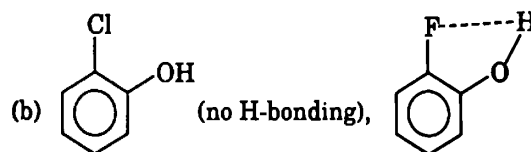
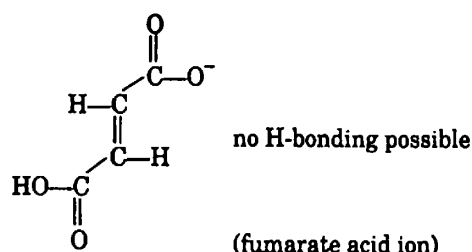
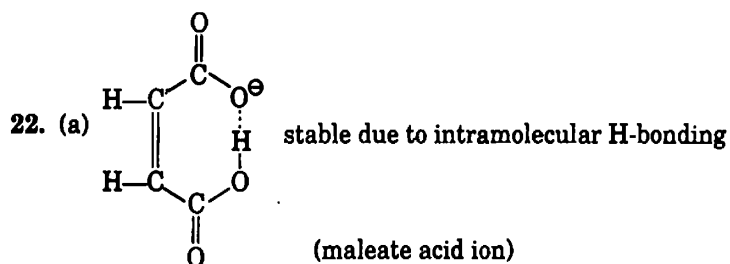
## Answers

1. (b)  $\text{O}_2^-$  with one unpaired electron as decided by M.O. theory.  
 2.  $\text{N}_2$  loses bonding electron hence, destabilised;  $\text{O}_2$  loses anti-bonding electron hence, stabilised.  
 3. (a) 2 (b) 2.5 (c) 3  
 $\text{CN}^-$  has the shortest bond-length.  
 4.  $\text{H}_2^+$  : B.O. = 0.5, paramagnetic

$\text{C}_2^+$  : B.O. = 1.5, paramagnetic  
 $\text{F}_2^+$  : B.O. = 1.5, paramagnetic  
 (Refer Table 2.10, 2.11)

5.  $\text{Li}_2^+ = \text{Li}_2^- < \text{Li}_2$   
 6. See text

7.  $F^-$ ,  $I^-$ ,  $Cl^-$  and  $H_2O$  are weak ligands, other are strong ligands.  
 8.  $NH_3$  forms deep blue coloured complex with  $Cu^{2+}$  and colour change appears rapidly. Acid neutralises  $NH_4OH$  (aq  $NH_3$ ) but reaction appears bit slowly.  
 9. (c)  
 10. (a)  $CO_2$  (b)  $HF$  (c)  $Cl_2$  (d)  $HOI$   
 11. Polar :  $ICl$ ,  $NO$ ,  $SO_2$ ,  $CH_2Cl_2$ ,  $OCS$  (due to electronegativity difference between the bonded atoms)  
 Non-polar :  $Cl_2$  (due to identical atom)  
 $BF_3$ ,  $XeF_4$  (due to symmetry)  
 12. 5.99 Debye 13. 84.4% 14. Higher dipole moment of  $OCS$   
 15. (I)  $Al_2O_3$  (II)  $ZnO$   
 16. Ether extracts  $LiCl$  (covalent) from mixture.  
 17. (a)  $AlN < MgO < NaF$  (b)  $CaF_2 < MgF_2 < AgF$   
 (c)  $AgI < AgBr < AgCl < AgF$   
 18.  $Cd^{2+}$  19. Due to decrease in ionic character.  
 20. (a)  $CH_3CH_2OH$  (b)  $CH_3NH_2$  (c)  $CH_3OH$   
 21.  $NH_3$ ,



H-bonding in *o*-fluorophenol decrease angle ( $< 60^\circ$ ) hence,  $\mu$  is increased.

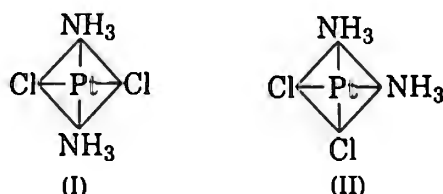
23. (a)  $NO_3^-$  (with three equivalent resonating structure)  
 (b)  $H-C \equiv O^-$  (with two equivalent resonating structures)  
 (c)  $CO_3^{2-}$   
 24.  $\cdot\ddot{N}::\dot{N}::\ddot{N}\cdot \longleftrightarrow :N::\dot{N}::\ddot{N}:^{2-} \longleftrightarrow ^{2-}::\ddot{N}::\dot{N}::N:$   
 25. It is due to resonating structures that all C—C bond lengths are equal.  
 26.  $O=C=C=C=O$ ,  $\bar{O}-C \equiv C-C=O^+$   
 27.  $7.015 \times 10^{20}$  energy levels in the 3s conduction band.  
 $7.015 \times 10^{20}$  electrons in the band.  
 28. (c) and (a) 29. See text 30. See text 31. See text



# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** The platinum-chlorine distance has been found to be 2.32 Å in several crystalline compounds. If this value applies to both of the compounds shown in Fig., what is the chlorine-chlorine distance in (a) structure I and (b) structure II?



*Plan* I and II are geometrical isomers and based on position of Cl-atoms, distance between them can be determined.

**Solution** (a) Given (Pt—Cl) distance = 2.32 Å

Since both Cl and Pt atoms are in straight line hence in (I) Cl—Cl distance

$$= 2 \times 2.32 \text{ Å}$$

$$= 4.64 \text{ Å}$$

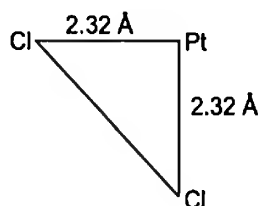
(b) In (II), Cl—Cl distance

$$= \sqrt{(2.32)^2 + (2.32)^2}$$

$$= 2.32\sqrt{2}$$

$$= 2.32 \times 1.414$$

$$= 3.28 \text{ Å}$$



**Problem 2.** The C—C single-bond distance is 1.54 Å. What is the distance between the terminal carbons in propane? Assume that the four bonds of any carbon atom are pointed towards the corners of a regular tetrahedron.

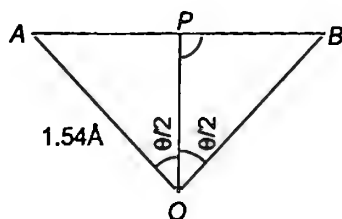
*Plan* Structure of propane is assumed to be tetrahedral with bond angle of  $\theta = 109^\circ 28'$ . Thus, from the value of  $\left(\frac{\theta}{2}\right)$  and sin values, distance between terminal C-atoms can be determined.

**Solution** Two terminal carbons can be assumed to be at A and B, while the central carbon at O. Then,

$$AB = 2AP$$

$$\frac{AP}{AO} = \sin\left(\frac{\theta}{2}\right)$$

But



$$= \sin\left(\frac{109^\circ 28'}{2}\right) \therefore \text{(in tetrahedral structure)}$$

$$\theta = 109^\circ 28'$$

$$= \sin(54^\circ 44')$$

$$\therefore AP = AO \sin(54^\circ 44')$$

$$= 1.54 \times 0.82 = 1.26 \text{ Å}$$

$$\therefore AB = 2AP = 2.52 \text{ Å}$$

**Problem 3.** The dipole moment of HBr is  $2.60 \times 10^{-30}$  C.m. and the interatomic spacing is 1.41 Å. What is the per cent ionic character of HBr?

*Plan* Per cent ionic character =  $\frac{\text{observed value}}{\text{theoretical value}} \times 100$

**Solution** Theoretical value of dipole moment of a 100% ionic character =  $e \times d$

$$= (1.60 \times 10^{-19} \text{ C}) (1.41 \times 10^{-10} \text{ m})$$

$$= 2.26 \times 10^{-29} \text{ C.m.}$$

$$\text{observed value of dipole moment} = 2.60 \times 10^{-30} \text{ C.m.}$$

$$\text{per cent ionic character} = \frac{\text{observed value}}{\text{theoretical value}} \times 100$$

$$= 2.60 \times \frac{2.60 \times 10^{-30}}{2.26 \times 10^{-29}} \times 100 = 11.5\%$$

**Problem 4.** A diatomic molecule has a dipole moment of 1.2 D. If its bond distance is 1.0 Å, what fraction of an electronic charge exists on each atom?

*Plan* Based on dipole moment of 1.2 D, electronic charge is calculated. This value is compared to theoretical value of charge ( $= 4.8 \times 10^{-10}$  esu).

**Solution** For a diatomic molecule dipole moment  $\mu = e \times d$

$$\therefore \text{electronic charge} = \frac{\mu}{d} = \frac{1.2 \times 10^{-18} \text{ esu cm}}{1.0 \times 10^{-8} \text{ cm}}$$

$$= 1.2 \times 10^{-10} \text{ esu}$$

$$\text{actual value of electronic charge} = 4.8 \times 10^{-10} \text{ esu}$$

$$\therefore \text{fraction of the electronic charge} = \frac{1.2 \times 10^{-10}}{4.8 \times 10^{-10}} = 0.25$$

**Problem 5.** At 300 K and 1.00 atm, the density of gaseous HF is 3.17 g/L. Explain the observation, and support your explanation by calculations.

**Plan** HF molecules are associated by H-bonding. Overall molecular weight of the associated molecule is determined, hence number of HF molecules associated can be predicted.

**Solution**

$$PV = nRT = \frac{w}{m} RT$$

$$\therefore P = \frac{w}{Vm} RT = \frac{dRT}{m}$$

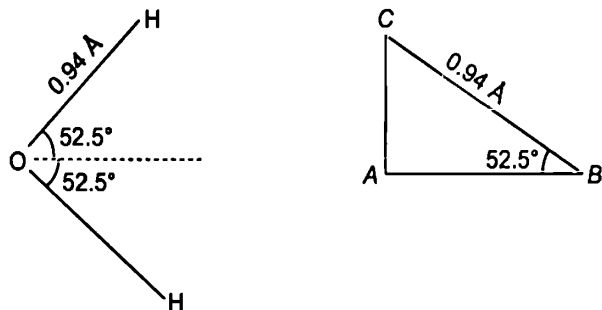
$$\therefore m \text{ (molecular weight)} = \frac{dRT}{P} = \frac{3.17 \times 0.0821 \times 300}{1}$$

$$= 78.08 \text{ g mol}^{-1}$$

But normal molecular weight of HF = 19 g mol<sup>-1</sup>.

Thus, four molecules of HF are associated in gaseous phase by hydrogen bonding, forming tetramer of molecular weight 78.08 g mol<sup>-1</sup>.

**Problem 6.** Dipole moment of H<sub>2</sub>O is 1.85 D. If bond angle is 105° and O—H bond length is 0.94 Å, determine magnitude of the charge on the oxygen atom in the water molecule.



**Plan** From the bond angle and vector moment  $\mu = e \times l$  Thus,  $e$  (charge) can be determined.

**Solution**

$$AB = BC \cos 52.5^\circ$$

$$= 0.94 \times 0.609 = 0.572 \text{ Å}$$

$$= 0.572 \times 10^{-8} \text{ cm}$$

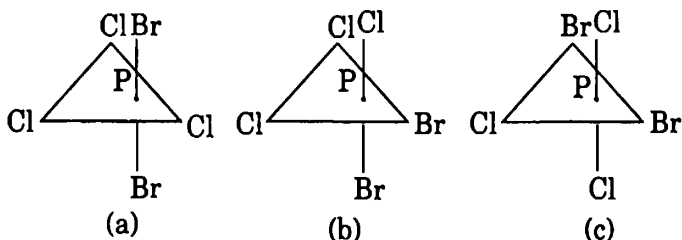
Also

$$\mu = e \times AB$$

$$\therefore e = \frac{\mu}{AB} = \frac{1.85 \times 10^{-18} \text{ esu cm}}{0.572 \times 10^{-8} \text{ cm}}$$

$$= 3.23 \times 10^{-10} \text{ esu}$$

**Problem 7.** Draw all the geometric isomers of  $\text{PBr}_2\text{Cl}_3$  molecule. State whether each isomer has a dipole moment.

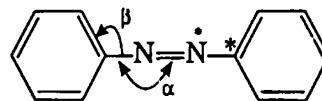


**Plan** Symmetrical molecules will have net dipole zero while unsymmetrical molecules will have dipoles.

**Solution** (a) is symmetrical hence no dipole. (b) and (c) have dipoles.

**Problem 8.** Azobenzene,  $(\text{C}_6\text{H}_5)_2\text{N}_2$ , is an important starting material in the production of dyes.

- (a) Describe the hybridisation scheme for the atoms marked with (\*).  
 (b) Indicate the value of the bond angles labelled  $\alpha$  and  $\beta$ .



**Plan** From the type of hybridisation, bond angles can be predicted.

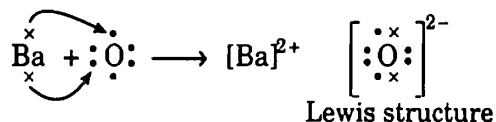
**Solution** (a) Each  $sp^2$  (b)  $\alpha = \beta = 120^\circ$

**Problem 9.** Write Lewis structure for the following compounds :

- (a) BaO (b)  $\text{MgCl}_2$  (c)  $\text{K}_2\text{S}$

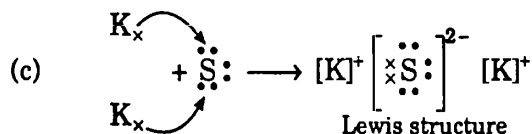
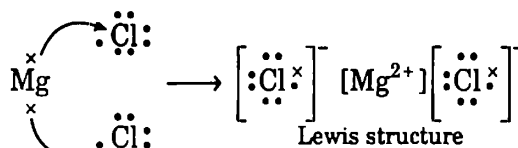
**Plan** Based on valence-shell electron-configuration, Lewis structure can be written.

**Solution** (a)  $\text{Ba} = [\text{Xe}]6s^2$  : two electrons excess to inert gas configuration; can lose two electrons.  
 $\text{O} = 1s^2 2s^2 2p^4$  : two electrons less than octet; can gain two electrons



- (b)  $\text{Mg} = [\text{Ne}]3s^2$  : two electrons excess to inert gas configuration; can lose two electrons.

$\text{Cl} = [\text{Ne}]3s^2 3p^5$  : one electron less than octet; two chlorine atoms gain two electrons lost by magnesium



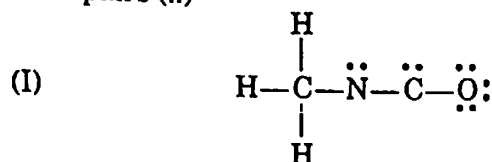
**Problem 10.** Applying the VSEPR theory, predict the shape of methyl isocyanate  $\text{CH}_3\text{NCO}$ .

**Plan** Using valence-shell electrons and Lewis structure, shape of  $\text{CH}_3\text{NCO}$  is predicted.

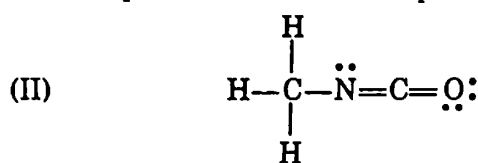
**Solution** Number of valence electrons

$$\begin{array}{ccccccc} \text{C} & \text{H}_3 & \text{N} & \text{C} & \text{O} \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ 4 & + & 3 & + & 5 & + & 4 & + & 6 & = & 22 \end{array}$$

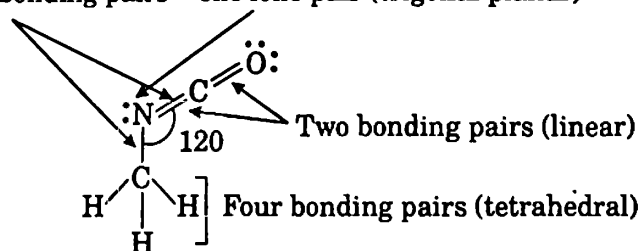
We assign structure I with six bond pairs (–) and five lone pairs (..)



But this structure lacks octet of N and C, hence by shift of electrons of lone pairs to bonding pairs, we write structure II in which each of atoms has completed octet (H with duplet).



Two bonding pairs    one lone pair (trigonal planar)



Again note here, we have not taken  $\pi$  bonds into account to decide shape of the molecule.

**Problem 11.** By the following method you can predict the geometrical shape of species with only one central atom, without first drawing the Lewis structure :

1. Total number of electron pairs  
= (number of valence electrons  $\pm$  electrons (for ionic) charge) / 2
2. Number of bond electron pairs = number of atoms – 1
3. Number of electron pairs around central atom  
= total number of electron pairs – 3 [number terminal atoms (except H)]
4. Number lone pair  
= (number of central electron pairs – number bond pair)

What is the shape of the following based on this method?

- (a)  $\text{PCl}_5$       (b)  $\text{NH}_3$       (c)  $\text{H}_2\text{O}$   
(d)  $\text{ClO}_3^-$       (e)  $\text{ICl}_4^-$

**Plan** We follow the steps given in the question to predict the shape.

**Solution** Solution is in the Table 2.15.

Table 2.15 Solution of Example 11

| Species                  | Steps                             |      |               |             | VSEPR notation          | Structure (Table 2.6) |
|--------------------------|-----------------------------------|------|---------------|-------------|-------------------------|-----------------------|
|                          | 1                                 | 2(X) | 3             | 4(E)        |                         |                       |
| (a) $\text{PCl}_5$       | $\frac{5 + (5 \times 7)}{2} = 20$ | 5    | $20 - 15 = 5$ | $5 - 5 = 0$ | $\text{AX}_5$           | trigonal bipyramidal  |
| (b) $\text{NH}_3$        | $\frac{5 + 3}{2} = 4$             | 3    | $4 - 0 = 4$   | $4 - 3 = 1$ | $\text{AX}_3\text{E}$   | trigonal pyramidal    |
| (c) $\text{H}_2\text{O}$ | $\frac{2 + 6}{2} = 4$             | 2    | $4 - 0 = 4$   | $4 - 2 = 2$ | $\text{AX}_2\text{E}_2$ | angular               |
| (d) $\text{ClO}_3^-$     | $\frac{7 + 18 + 1}{2} = 13$       | 3    | $13 - 9 = 4$  | $4 - 3 = 1$ | $\text{AX}_3\text{E}$   | pyramidal             |
| (e) $\text{ICl}_4^-$     | $\frac{7 + 28 + 1}{2} = 18$       | 4    | $18 - 12 = 6$ | $6 - 4 = 2$ | $\text{AX}_4\text{E}_2$ | square planar         |

All the structures determined by this new method is similar to that used by VSEPR theory and is widely acceptable.

**Problem 12.** In certain polar solvents  $\text{PCl}_5$  undergoes an ionisation reaction in which  $\text{Cl}^-$  ion leaves one  $\text{PCl}_5$  molecule and attaches itself to another.



What are the changes in the geometrical shapes that occur in this ionisation?

**Plan** We follow the steps as given by Example 11.

## Solution

| Steps                                            | $\text{PCl}_5$          | $\text{PCl}_4^+$            | $\text{PCl}_6^-$            |
|--------------------------------------------------|-------------------------|-----------------------------|-----------------------------|
| (1) Total number of electron pairs               | $\frac{5 + 35}{2} = 20$ | $\frac{5 + 28 - 1}{2} = 16$ | $\frac{5 + 42 + 1}{2} = 24$ |
| (2) Number of bonded electron pairs              | 5                       | 4                           | 6                           |
| (3) Number of electron pairs around central atom | $20 - 15 = 5$           | $16 - 12 = 4$               | $24 - 18 = 6$               |
| (4) Number of lone pairs                         | 0                       | 0                           | 0                           |
| (5) VSEPR notation                               | $\text{AX}_5$           | $\text{AX}_4$               | $\text{AX}_6$               |
| (6) Structure                                    | trigonal bipyramidal    | tetrahedral                 | octahedral                  |

If you manage to determine type of hybridisation of P atom in each, then structure can be decided, but this will also require whether lone pair is present or not.

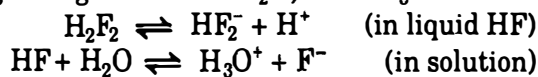
$\text{PCl}_5$   $sp^3d$  trigonal bipyramidal

$\text{PCl}_4^+$   $sp^3$  tetrahedral

$\text{PCl}_6^-$   $sp^3d^2$  octahedral

**Problem 13.** The  $\text{HF}_2^-$  ion exists in the solid state and also in liquid HF solution, but not in dilute aqueous solution. Explain.

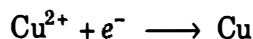
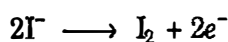
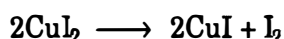
**Solution** In the solid state and in liquid HF, the  $\text{HF}_2^-$  ion is held together by hydrogen bonding. In aqueous solutions, there is hydrogen bonding, but each HF molecule being stronger acid than  $\text{H}_2\text{O}$ , forms  $\text{H}_3\text{O}^+$  and  $\text{F}^-$ .



**Problem 14.** Copper (II) iodide is unstable even at ordinary temperature. Explain.

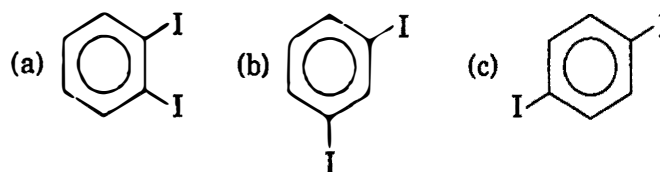
**Plan** Explanation can be made in terms of polarisation of cation by anion and vice-versa as predicted by Fajan's rule.

**Solution** The  $\text{Cu}^{2+}$  ion with a 17-electron outer-shell and a comparatively small radius (0.08 nm) has a strong polarising power, while the iodide ion with a larger radius ( $r = 0.22$  nm) has a high polarisability. Hence, the polarisation of the  $\text{I}^-$  by the  $\text{Cu}^{2+}$  leads to the complete transition of an electron from the anion to the cation : the  $\text{Cu}^{2+}$  ion is thus reduced to  $\text{Cu}^+$  ion and  $\text{I}^-$  is oxidised to free iodine. The compound  $\text{CuI}_2$  therefore, does not exist.



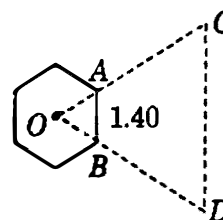
**Problem 15.** Assuming the additivity of covalent radii in the C—I bond, what would be the iodine-iodine distance in each of the diiodobenzene? Assume that the ring is regular hexagon and that each C—I bond lies on a line through the centre of the hexagon. (Take C—C

bond-length = 1.40 Å radius of iodine atom = 1.33 Å, radius of carbon atom = 0.77 Å)



**Plan** In o- m- and p-isomers, bond angles are respectively  $60^\circ$ ,  $120^\circ$  and  $180^\circ$  hence, distance between two-atoms can be calculated.

**Solution** (a) I-atoms are at C and D positions.  $CD = ?$

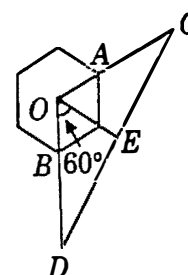


Also,  $\triangle OCD$  is equilateral triangle.

$$\begin{aligned} CD &= OC = OA + AC \\ &= 1.40 + 1.33 + 0.77 \\ &= 3.50 \text{ Å} \end{aligned}$$

(AC is the sum of radii of carbon and iodine and  $OA = AB$ )

(b)  $CD = 2DE$



But

$$\frac{DE}{OD} = \sin 60^\circ$$

$$\begin{aligned} DE &= OD \sin 60^\circ \\ &= (OB + BD) \sin 60^\circ \\ &= (1.40 + 0.77 + 1.33) \sin 60^\circ \end{aligned}$$

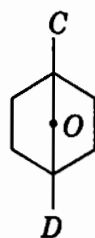
$$= 3.50 \times \frac{\sqrt{3}}{2} = 3.03 \text{ \AA}$$

$$\therefore CD = 6.06 \text{ \AA}$$

(BD = AC as in (a))

$$(c) \quad OC = OD = 3.50 \text{ \AA}$$

$$\therefore CD = 2 \times 3.50 = 7.0 \text{ \AA}$$



$$\begin{aligned} &= 135 - \sqrt{104 \times 38} \\ &= 135 - 62.86 \\ &= 72.14 \text{ kcal mol}^{-1} \end{aligned}$$

**Problem 16.** Calculate the electronegativity of chlorine from the bond energy of Cl—F bond ( $61 \text{ kcal mol}^{-1}$ ), F—F bond ( $38 \text{ kcal mol}^{-1}$ ) and Cl—Cl bond ( $58 \text{ kcal mol}^{-1}$ ), and electronegativity of fluorine  $4.0 \text{ eV}$ .

**Plan** Based on Pauling's scale :

$$(\text{EN})_{\text{F}} - (\text{EN})_{\text{Cl}} = k\sqrt{\Delta} = 0.208\sqrt{\Delta}$$

where  $\Delta$  is resonance energy and  $k$  is the conversion factor (which is 0.208 for converting kcal into eV).

$$\text{Solution } \Delta = (\text{BE})_{\text{Cl-F}} - \sqrt{(\text{BE})_{\text{Cl-Cl}} (\text{BE})_{\text{F-F}}}$$

$$= 61 - \sqrt{58 \times 38}$$

$$= 61 - 46.95 = 14.05 \text{ kcal}$$

$$(\text{EN})_{\text{Cl}} = (\text{EN})_{\text{F}} - 0.208\sqrt{\Delta}$$

$$= 4.0 - 0.208\sqrt{14.05}$$

$$= 4.0 - 0.78 = 3.22 \text{ eV}$$

**Problem 17.** Bond energy of H—H, F—F and H—F bonds are 104, 38 and  $135 \text{ kcal mol}^{-1}$  respectively. Calculate resonance energy in the H—F molecule.

**Plan** As in Problem 16.

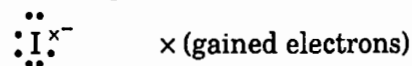
**Solution** Resonance energy

$$\Delta_{\text{H-F}} = (\text{BE})_{\text{H-F}} - \sqrt{(\text{BE})_{\text{H}_2} (\text{BE})_{\text{F}_2}}$$

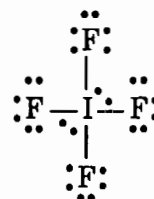
**Problem 18.** Calculate the steric numbers for iodine in  $(\text{IF}_4^-)$  and for bromine in  $(\text{BrO}_4^-)$ .

**Plan**  $S_N = (\text{Bonding atom} + \text{Lone pairs})$

**Solution** The central  $\text{I}^-$  has eight valence electrons



Each F atom has seven valence electrons of its own and needs to one of the electrons from  $\text{I}^-$  to attain noble-gas configuration ( $s^2 p^6$ ). Thus, four, of the  $\text{I}^-$  valence electrons take part in covalent bonds, leaving the remaining four to form two lone pairs. Thus,



$$S_N = 4 (\text{bonded atoms}) + 2 (\text{lone pairs}) = 6$$

The central  $\text{Br}^-$  has also eight electrons. In  $\text{BrO}_4^-$ , each oxygen atom needs to share two of electrons from  $\text{Br}^-$  to attain noble-gas configurations thus all the electrons are used in bonding and no lone pair exists.

$$\text{Thus, } S_N = 4 (\text{bonded pair}) + 0 (\text{lone pair}) = 4.$$

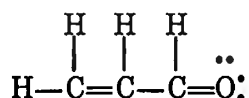
# Master Exercises

## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

1. Predict whether the molecules  $\text{NH}_3$  and  $\text{SF}_6$  will have dipole moments.

2. Acrolein is the starting material for certain plastics



- (a) Which bonds in the molecule are polar and which are non-polar?
  - (b) Which is the most polar bond in the molecule? Which is the most negative atom of this bond?
3. Consider the nitrogen—oxygen bond lengths in  $\text{NO}_2^+$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ . In which ion is the bond predicted to be longest? In which is it predicted to be the shortest?

4. Explain why the species I in each set has larger bond angle than II?

I

II

- |                    |               |
|--------------------|---------------|
| (a) $\text{CH}_4$  | $\text{NH}_3$ |
| (b) $\text{OCl}_2$ | $\text{OF}_2$ |
| (c) $\text{NH}_3$  | $\text{NF}_3$ |
| (d) $\text{NH}_3$  | $\text{PH}_3$ |

5. Explain why the valence bond structure of carbon monoxide is best described as



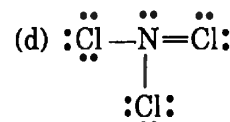
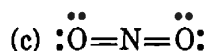
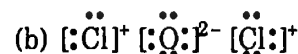
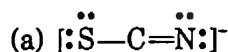
with a dative bond from oxygen atom to the less electronegative carbon atom.

6. The bond dissociation energy of  $\text{C}_2$  ( $599 \text{ kJ mol}^{-1}$ ) decreases slightly on forming  $\text{C}_2^+$  ( $513 \text{ kJ mol}^{-1}$ ) and increases greatly on forming  $\text{C}_2^-$  ( $818 \text{ kJ mol}^{-1}$ ). Why is the change much greater for the addition of an electron?

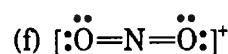
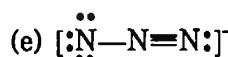
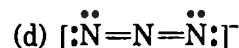
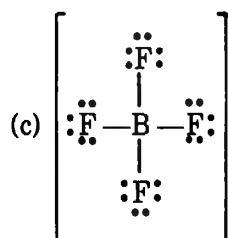
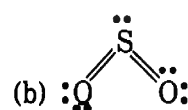
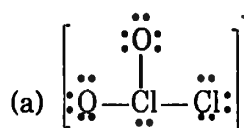
### Analytical Questions

#### Ionic, Covalent and Coordinate Bonding

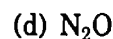
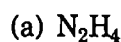
1. Indicate what is wrong with each of the following Lewis structures? Replace each with a more acceptable structure.



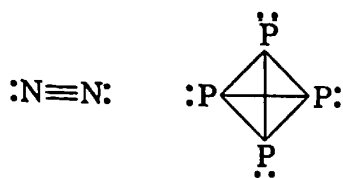
2. Assign formal charges to the following species. If there are no formal charges present for certain of these species, so indicate



3. In which of the following molecules would you expect the nitrogen-to-nitrogen bond to be the shortest?



4. The common forms of N and P are  $\text{N}_2$  and  $\text{P}_4$  respectively.



Using the following data, explain why the stable forms are  $\text{N}_2$ , not  $\text{N}_4$ ; and  $\text{P}_4$  not  $\text{P}_2$ ?

Mean bond enthalpy, ( $\text{kJ mol}^{-1}$ ).

|                          |     |                     |     |
|--------------------------|-----|---------------------|-----|
| $\text{N}\equiv\text{N}$ | 946 | $\text{P}=\text{P}$ | 481 |
| $\text{N}-\text{N}$      | 160 | $\text{P}-\text{P}$ | 215 |

5. A sample of lead (II) bromide,  $\text{PbBr}_2$ , was placed in a crucible. The ends of two carbon electrodes were put in the solid and connected to a lamp and power pack. At first the lamp did not light, but when the bromide was heated and began to melt the lamp began to glow. Explain these observations.

6. What are two types of bonds present in  $\text{B}_2\text{H}_6$ ?

7. The experimentally determined  $\text{N}-\text{F}$  bond length in  $\text{NF}_3$  is greater than the sum of the single bond covalent bond radii of N and O. Explain.

8. The correct order of increasing  $\text{C}-\text{O}$  bond length of  $\text{CO}$ ,  $\text{CO}_3^{2-}$ ,  $\text{CO}_2$  is

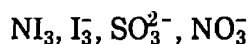
- (a)  $\text{CO}_3^{2-} < \text{CO}_2 < \text{CO}$       (b)  $\text{CO}_2 < \text{CO}_3^{2-} < \text{CO}$   
 (c)  $\text{CO} < \text{CO}_3^{2-} < \text{CO}_2$       (d)  $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$

9. In the dichromate dianion

- (a) 4  $\text{Cr}-\text{O}$  bonds are equivalent  
 (b) 6  $\text{Cr}-\text{O}$  bonds are equivalent  
 (c) all  $\text{Cr}-\text{O}$  bonds are equivalent  
 (d) all  $\text{Cr}-\text{O}$  bonds are non-equivalent

### Hybridization/Shape of Molecules

10. Two of the following species have the same shape. Which are these two? What is their shape? What are the shapes of the other two?



11. Write plausible Lewis structures for the following molecules

- (a)  $\text{H}_2\text{NOH}$       (b)  $\text{N}_2\text{F}_2$   
 (c)  $\text{HONO}$       (d)  $\text{H}_2\text{NNO}_2$

12.  $\text{PF}_5$  and  $\text{BrF}_5$  appear similar formulae, but structures are different, explain.

13.  $\text{ClF}_2^-$  ion is linear but  $\text{ClF}_2^+$  is bent. Describe hybridisation schemes for the central Cl atom to account for this structure difference.

14. The hyponitrite ion,  $^-\text{O}-\text{N}=\text{N}-\text{O}^-$ , exists in solid compounds as the *trans* isomer. Using VB theory, explain why *cis* – *trans* isomers might be expected for this ion?

15. A molecular compound is composed of 60.4% Xe, 21.1% O and 17.5% F, by mass. If the molecular weight is 217.3 u, what is the molecular formula? Predict the molecular geometry using the VSEPR

model. Describe the bonding, using valence bond theory.

16. I. Which one of the following molecules is planar?

- (a)  $\text{NF}_3$       (b)  $\text{NCl}_3$   
 (c)  $\text{PH}_3$       (d)  $\text{BF}_3$

II. What is the type and number of bonds between the two carbon atoms in  $\text{CaC}_2$ ?

17. Each of the following compounds has a nitrogen-nitrogen bond

$\text{N}_2$ ,  $\text{N}_2\text{H}_4$ ,  $\text{N}_2\text{F}_2$ . Match each compound with one of the following bond lengths

1.10 Å, 1.22 Å, 1.45 Å. Describe the geometry about one of the N atoms in each compound. Why hybrid orbitals are needed to describe the bonding in valence bond theory?

18. "EI" is the general symbol for a representative element. In each case, name the probable element EI.

- (a)  $\begin{bmatrix} \text{O}-\text{EI}-\text{O} \\ | \\ \text{O} \end{bmatrix}^-$       (b)  $\text{H}-\text{O}-\text{EI}=\text{O}$   
 (c)  $\begin{bmatrix} \text{O} \\ | \\ \text{O}-\text{EI}-\text{O} \\ | \\ \text{O} \end{bmatrix}^{2-}$       (d)  $\begin{array}{c} \text{H}-\text{O}-\text{EI}-\text{H} \\ | \\ \text{H} \end{array}$

19. A monomeric anhydrous complex of Co gives the following results:

|               |          |                      |          |
|---------------|----------|----------------------|----------|
| Co            | : 21.24% | $\text{SO}_4^{2-}$   | : 34.65% |
| $\text{NH}_3$ | : 24.77% | $\text{H}_2\text{O}$ | : 6.53%  |
| $\text{Cl}^-$ | : 12.81% |                      |          |

(Co : 58, Cl = 35.5, S = 32, N = 14); Z (Co = 27)

The compound is diamagnetic and gives white ppt with  $\text{BaCl}_2$ . What is its empirical formula? What is its structure?

[Hint : Determine molar ratio. Since complex is diamagnetic, hence, cobalt has no unpaired electron.  $\text{SO}_4^{2-}$  is outside coordinate sphere since it gives white ppt with  $\text{BaCl}_2$ .]

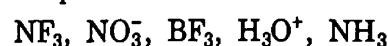
20.  $\text{N}(\text{CH}_3)_3$  is pyramidal but  $\text{N}(\text{SiH}_3)_3$  is planar. Explain.

21. Fill in the blanks

- (a) The shape of  $\text{CH}_3^+$  is .....  
 (b) The valence atomic orbitals on C in silver acetylide is ..... hybridised.

22. Using the VSEPR theory, identify the type of hybridisation and draw the structure of  $\text{OF}_2$ . What are the oxidation states of O and F?

23. Among the following species identify the isostructural pairs



## 24. I. Select correct alternate

Among  $\text{KO}_2$ ,  $\text{AlO}_2^-$ ,  $\text{BaO}_2$  and  $\text{NO}_2^+$ , unpaired electron is present in :

- (a)  $\text{NO}_2^+$  and  $\text{BaO}_2$       (b)  $\text{KO}_2$  and  $\text{AlO}_2^-$   
 (c)  $\text{KO}_2$  only      (d)  $\text{BaO}_2$  only

II. Among  $\text{N}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{I}_3^+$  and  $\text{I}_3^-$ , the linear species are ..... and .....

III. The angle  $\text{P}-\text{P}-\text{P}$  in  $\text{P}_4$  molecule is .....

25. What is the geometry and the type of hybrid orbital present about the central atom in  $\text{BF}_3$ ?

26. Interpret the non-linear shape of  $\text{H}_2\text{S}$  molecule and non-linear shape of  $\text{PCl}_3$  using VSEPR theory.

27. Discuss the hybridisation of carbon atoms in allene ( $\text{C}_3\text{H}_4$ ) and show that  $\pi$ -orbital overlap.

## Select the correct alternate (Q. 28 to 29)

28. The geometry of  $\text{Ni}(\text{CO})_4$  and  $\text{Ni}(\text{PH}_3)_2\text{Cl}_2$  are

- (a) both square planar  
 (b) tetrahedral and square planar  
 (c) both tetrahedral  
 (d) square planar and tetrahedral

29. In the compound  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{CH}$  the  $\text{C}_2-\text{C}_3$  bond is of the type

- (a)  $sp-sp^2$       (b)  $sp^3-sp^3$   
 (c)  $sp-sp^3$       (d)  $sp^2-sp^3$

30. Deduce the structure of  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  considering the hybridisation of the metal ion. Calculate the magnetic moment (spin only) of the species.

## MO Theory

31. Suggest reasons why the following do not exist as stable molecules?

- (a)  $\text{H}_3$       (b)  $\text{HHe}$   
 (c)  $\text{He}_2$       (d)  $\text{H}_3\text{O}$

32. Write MO diagram of (a)  $\text{CN}^+$  and (b)  $\text{BN}$ .

33. What is the molecular orbital configuration of  $\text{HeH}^+$ ? Do you expect the ion to be stable.

34. (a) When  $\text{N}_2$  goes to  $\text{N}_2^+$ , the  $\text{N}-\text{N}$  bond distance ... and when  $\text{O}_2$  goes to  $\text{O}_2^+$ ,  $\text{O}-\text{O}$  bond distance ...

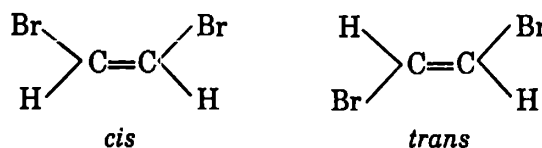
(b) Write MO electron distribution of  $\text{O}_2$ . Specify its bond order and magnetic property.

## Dipole Moment

35. Estimate the per cent ionic character of the  $\text{HBr}$  molecule, given that the dipole moment ( $\mu$ ) is 0.79 D and  $\text{HBr}$  bond length 151 pm.

36. (a) Draw Lewis structure for nitrosyl fluoride  $\text{FNO}$ .  
 (b) What is the geometrical shape?  
 (c) Explain why the measured resultant dipole moment for  $\text{FNO}$ , 1.81 D, is so much larger than the value for nitryl fluoride,  $\text{NO}_2\text{F}$  (0.47 D)?

37. Explain how the dipole moment could be used to distinguish between the *cis* and *trans* isomers of 1,2-dibromoethene?



38. The length of the dipole of  $\text{HF}$  molecule is  $4 \times 10^{-11}$  m. Calculate the dipole moment in coulomb-metres and in debyes.

39. Two substances A and B having the same molecular formula,  $\text{C}_4\text{H}_8\text{O}$ , were examined in the gaseous state by electron diffraction. The carbon-oxygen distance was found to be 1.43 Å in the compound A and 1.24 Å in compound B. What can you conclude about the structure of these two compounds?

40. The  $\text{N}_2\text{F}_2$  molecule can exist in either of the following two forms:



- (a) What is the hybridisation of N in the molecule?  
 (b) Which structure has a dipole moment?

41. The dipole moment of  $\text{HCN}$  molecule is 2.9 D. Calculate the length of the dipole.

42. The dipole moment of the  $\text{NH}_3$  molecule is 1.48 D. Calculate the length of the dipole. Can the molecule be assumed to have the shape of a regular triangle.

43. I. Arrange (A) toluene, (B) *m*-dichlorobenzene, (C) *o*-dichlorobenzene and (D) *p*-dichlorobenzene in order of increasing dipole moment.

II. Select the correct alternate :

The geometry of  $\text{H}_2\text{S}$  and its dipole moment are

- (a) angular and non-zero    (b) angular and zero  
 (c) linear and non-zero    (d) linear and zero

## Fajan's Rule/Lattice Energy

44. Compare the stability (in the solid state) of the following pairs of compounds:

- (a)  $\text{LiF}$  and  $\text{LiF}_2$       (b)  $\text{Cs}_2\text{O}$  and  $\text{CsO}$   
 (c)  $\text{CaBr}_2$  and  $\text{CaBr}_3$

45. Assume the following bonds in order of increasing ionic character:

C to H, F to H, Br to H, Na to I, K to F, Li to Cl

46. Explain.

- (a)  $\text{AuCl}_3$  is less stable than  $\text{AuCl}$  and  $\text{PbCl}_4$  is less stable than  $\text{PbCl}_2$ .  
 (b)  $\text{K}_2\text{CO}_3$  melts at  $890^\circ\text{C}$  without decomposing while  $\text{Ag}_2\text{CO}_3$  decomposes at  $220^\circ\text{C}$ .  
 (c)  $\text{BaCl}_2$  ionises in aqueous solution while  $\text{HgCl}_2$  does not (or very smaller).



- (d) The ionic radii of  $\text{Na}^+$  and  $\text{Cu}^+$  are the same (0.098 nm) but melting point of  $\text{NaCl}$  ( $801^\circ\text{C}$ ) is much higher than that of  $\text{CuCl}$  ( $430^\circ\text{C}$ ).

47. Anhydrous  $\text{AlCl}_3$  is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution.

Ionisation energy for  $\text{Al} = 5137 \text{ kJ mol}^{-1}$

$\Delta H_{\text{hydration}} (\text{Al}^{3+}) = -4665 \text{ kJ mol}^{-1}$

$\Delta H_{\text{hydration}} (\text{Cl}^-) = -381 \text{ kJ mol}^{-1}$

### Hydrogen Bonding/Metallic Bonding/General

48. I. There is no S—S bond in :

- (a)  $\text{S}_2\text{O}_4^{2-}$  (b)  $\text{S}_2\text{O}_5^{2-}$   
(c)  $\text{S}_2\text{O}_3^{2-}$  (d)  $\text{S}_2\text{O}_7^{2-}$

- II. Out of  $\text{Ni}(\text{CO})_4$ ,  $\text{Ni}(\text{CN})_4^{2-}$  and  $\text{NiCl}_4^{2-}$  select paramagnetic and diamagnetic.

- III. What is the type of hybridisation of  $\text{C}_2$ — $\text{C}_3$  single bond in  $\text{HC}\equiv\text{C}-\text{CH}=\text{CH}_2$ ?

- IV. Out of  $\text{SnCl}_2$ ,  $\text{NCO}^-$ ,  $\text{CS}_2$ ,  $\text{NO}_2^+$  and  $\text{SO}_2$  select the one with linear structure.

- V. What is increasing strength of hydrogen bonding ( $X \cdots \text{H}-X$ ) ( $X = \text{O}, \text{S}, \text{F}, \text{Cl}, \text{N}$ )?

49. I. What is type of hybrid orbitals used by the chloride in  $\text{ClO}_2^-$ ?

- II. The cyanide ion,  $\text{CN}^-$  and  $\text{N}_2$  are isoelectronic. But in contrast to  $\text{CN}^-$ ,  $\text{N}_2$  is chemically inert because of .....

- III. The maximum possible number of hydrogen bonds a water molecule can form is .....

- IV. Which of the following have identical bond order

$\text{CN}^-$ ,  $\text{O}_2^-$ ,  $\text{NO}^+$ ,  $\text{CN}^+$ ?

- V. Which has highest dipole moment out of

- (a) 2, 2-dimethyl propane  
(b) *trans*-2-pentene  
(c) *cis*-3-hexene  
(d) 2,2,3,3-tetramethyl butane?

50. (I) The structure of the enolic form of  $\text{CH}_3-\text{CO}-\text{CH}_2-\text{CO}-\text{CH}_3$  with intra-molecular H-bonding is .....

- (II) Pick out the isoelectronic structure from the following:

$\text{CH}_3^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{NH}_3$ ,  $\text{CH}_3^-$

51. Explain why *o*-hydroxybenzaldehyde is a liquid at room temperature while *p*-hydroxybenzaldehyde is high melting solid?

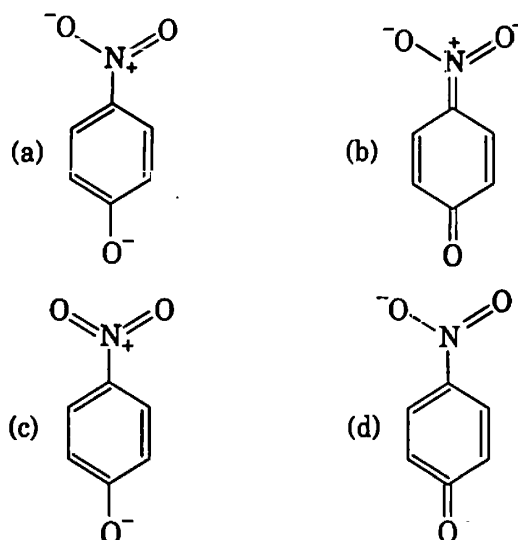
### Resonance

52.  $\text{NO}_2$  gas is paramagnetic at room temperature. On cooling below  $0^\circ\text{C}$ , its molecular weight increases and it loses its paramagnetism. When it is reheated, the behaviour is reversed. Explain. How does this phenomenon differ from resonance?

53. The central C—C bond in 1,3-butadiene is shorter than that of *n*-butane. Explain.

54. Select the correct alternate :

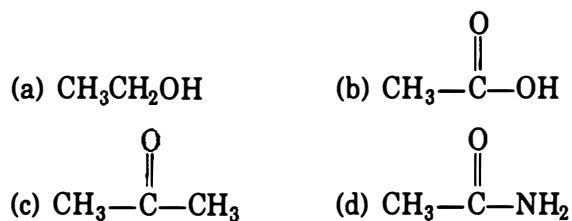
The most unlikely representation of resonance structure of *p*-nitrophenoxide is:



### NCERT Problems

- Two *p*-orbitals from one atom and two *p* orbitals from another atom are combined to form molecular orbitals. How many MOs will result from this combination? Explain.
- Show the shapes of bonding and anti-bonding MOs formed by combination of (a) two *s* orbitals (b) two *p* orbitals (side to side).
- How do the bonding and anti-bonding MOs formed from a given pair of AOs compare to each other with respect to (a) energy (b) presence of nodes (c) internuclear electron density?
- Arrange the following species in order of increasing stability :  $\text{Li}_2$ ,  $\text{Li}_2^+$ ,  $\text{Li}_2^-$ . Justify your choice with a molecular orbital energy level diagram.
- Use molecular orbital theory to explain why the  $\text{Be}_2$  molecule does not exist?
- Explain why the bond order of  $\text{N}_2$  is greater than  $\text{N}_2^+$ , but the bond order of  $\text{O}_2$  is less than that of  $\text{O}_2^+$ ?
- Compare the relative stability of the following species and indicate their magnetic properties (diamagnetic or paramagnetic);  $\text{O}_2$ ,  $\text{O}_2^+$ ,  $\text{O}_2^-$  (superoxide),  $\text{O}_2^{2-}$  (peroxide ion).
- Explain the significance of bond order. Can bond order be used for quantitative comparisons of the strength of chemical bonds.
- What is the energy gap in band theory? Compare its size in conductors, semiconductors and insulators.

10. Which of the following substances will exhibit H-bonding? Draw the H bonds between two molecules of the substance where appropriate.



11. How can one non-polar induce a dipole in a nearby non-polar molecule?

12. What type(s) of intermolecular forces exist between the following pairs? (a) HBr and  $\text{H}_2\text{S}$ , (b)  $\text{Cl}_2$  and  $\text{CBr}_4$ , (c)  $\text{I}_2$  and  $\text{NO}_3^-$ , and (d)  $\text{NH}_3$  and  $\text{C}_6\text{H}_6$ ?

**[Hint :** To identify intermolecular forces, it is useful to classify the species being considered as (1) non-polar molecules, (2) polar molecules, and (3) ions. Keep in mind that dispersion forces exist between all species.]

## Exercise 2

### (Stage 2 : High Skill Problem Solving)

#### Only One Option Correct

1. In which of the following molecules would you expect the nitrogen-to-nitrogen bond to be the shortest?



2. One of the following ions has a trigonal planar shape



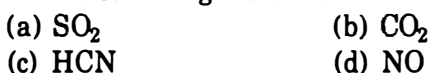
3. Which of the following molecules or ions is not linear?



4. The formal charge of the O atoms in the ion  $[\ddot{\text{O}}=\text{N}=\ddot{\text{O}}:]^+$  is



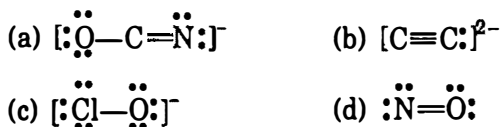
5. All the following molecules are linear except one



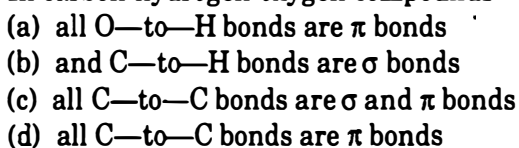
6. All the following molecules are polar except one



7. Correct Lewis structure is



8. In carbon-hydrogen-oxygen compounds



9. The hybridisation scheme for the central atom includes a d-orbital contribution in



10. Delocalised molecular orbitals are found in



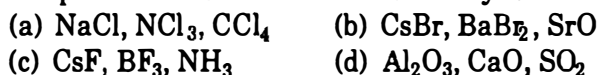
11. A substance in which large energy gap separates the valence and conduction band is a



12. Which of the following has the highest percentage of ionic character in its bonding?



13. In which of the following sets do all the three compounds have bonds that are mainly ionic?



14. Which of the following salts is not soluble in water?



15. Which of the following is an electron-deficient compound?



16. Which of the following is non-polar but contains polar bonds?



17. Following consists of discrete polar molecules at room temperatures



18. One of the following is least volatile



19. Which of the following does not obey 18-electron rule?



20. Which of the following will have the molecular shape of a trigonal bipyramid?  
 (a)  $\text{PF}_3\text{Cl}_2$  (b)  $\text{IF}_5$   
 (c)  $\text{BrF}_5$  (d)  $\text{SbF}_2^{2-}$
21. Which of the following diatomic molecules would be stabilised by the removal of an electron?  
 (a)  $\text{C}_2$  (b)  $\text{CN}$   
 (c)  $\text{N}_2$  (d)  $\text{O}_2$
22. The expected spin-only magnetic moments (BM) for  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{FeF}_6]^{3-}$  respectively are  
 (a) 1.73 and 1.73 (b) 1.73 and 5.92  
 (c) 0.0 and 1.73 (d) 0.00 and 5.92
23. Which of the following species/molecules has a planar geometry?  
 (a)  $\text{Ni}(\text{CO})_4$  (b)  $\text{SF}_4$   
 (c)  $\text{CoCl}_4^{2-}$  (d)  $\text{XeF}_4$
24.  $\text{O}_2$  molecule is paramagnetic due to presence of  
 (a) two unpaired electrons in anti-bonding MO  
 (b) one unpaired electron in anti-bonding MO  
 (c) two unpaired electrons in bonding MO  
 (d) one unpaired electron in bonding MO
25. Resonance is not observed in  
 (a)  $\text{CO}_2$  (b)  $\text{NH}_3$   
 (c)  $\text{SO}_3$  (d)  $\text{NO}_2$
26. Which of the following can provide an electron pair for the formation of a coordinate covalent bond?  
 (a)  $\text{H}^+$  (b)  $\text{H}^-$   
 (c)  $\text{H}_2$  (d)  $\text{He}^{2+}$
27. Allyl cyanide has  
 (a) 9 sigma bonds and 4 pi bonds  
 (b) 9 sigma bonds, 3 pi bonds and 1 lone pair  
 (c) 8 sigma bonds and 5 pi bonds  
 (d) 8 sigma bonds, 3 pi bonds
28. (C—Cl) bond in  $\text{CH}_2=\text{CH}-\text{Cl}$  (vinyl chloride) is stabilised in the same way as in  
 (a) benzyl chloride (b) benzoyl chloride  
 (c) chlorobenzene (d) allyl chloride
29. Arrange the following compounds in increasing dipole moment : toluene (I), *m*-chlorobenzene (II), *o*-dichlorobenzene (III), *p*-dichlorobenzene (IV)  
 (a)  $\text{I} < \text{IV} < \text{II} < \text{III}$  (b)  $\text{IV} < \text{I} < \text{II} < \text{III}$   
 (c)  $\text{IV} < \text{I} < \text{III} < \text{II}$  (d)  $\text{IV} < \text{II} < \text{I} < \text{III}$
30. When  $\text{N}_2^+$  is formed from  $\text{N}_2$  bond-order ..... and when  $\text{O}_2^+$  is formed from  $\text{O}_2$  bond-order ..... :  
 (a) increases  
 (b) decreases  
 (c) increases, decreases  
 (d) decreases, increases
31. Which of the following is most polar bond ?  
 (a)  $\text{Cl}-\text{Cl}$  (b)  $\text{N}-\text{F}$   
 (c)  $\text{C}-\text{F}$  (d)  $\text{O}-\text{F}$
32. The molecules that will have dipole moments are  
 (a) 1,2-dichloro benzene (b) *cis*-3-hexene  
 (c) *trans*-2-pentene (d) all of these
33. Which of the following have identical bond order?  
 (I)  $\text{CN}^-$  (II)  $\text{O}_2^-$   
 (III)  $\text{NO}^+$  (IV)  $\text{CN}^+$   
 (a) I, III (b) II, IV  
 (c) I, II, III (d) I, IV
34.  $\text{C}_2-\text{C}_3$  sigma single bond in vinyl acetylene  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$  is due to overlapping of  
 (a)  $sp-sp$  (b)  $sp^2-sp^2$   
 (c)  $sp-sp^2$  (d)  $sp^2-sp$
35. C—H bond distance is the longest in  
 (a)  $\text{C}_2\text{H}_2$  (b)  $\text{C}_2\text{H}_4$   
 (c)  $\text{C}_2\text{H}_6$  (d)  $\text{C}_2\text{H}_2\text{Br}_2$
36. Among the following species, identify the isostructural pairs  
 $\text{NF}_3, \text{NO}_3^-, \text{BF}_3, \text{H}_3\text{O}^+, \text{HN}_3$   
 (a)  $[\text{NF}_3, \text{NO}_3^-]$  and  $[\text{BF}_3, \text{H}_3\text{O}^+]$   
 (b)  $[\text{NF}_3, \text{HN}_3]$  and  $[\text{NO}_3^-, \text{BF}_3]$   
 (c)  $[\text{NF}_3, \text{H}_3\text{O}^+]$  and  $[\text{NO}_3^-, \text{BF}_3]$   
 (d)  $[\text{NF}_3, \text{H}_3\text{O}^+]$  and  $[\text{HN}_3, \text{BF}_3]$
37.  $\text{Mg}_2\text{C}_3$  reacts with water forming propyne.  $\text{C}_3^{4-}$  has  
 (a) two sigma and two pi bonds  
 (b) three sigma and one pi bonds  
 (c) two sigma and one pi bonds  
 (d) two sigma and three pi bonds
38. Which of the following statements is correct for  $\text{CsBr}_3$ ?  
 (a) It is covalent compound  
 (b) It contains  $\text{Cs}^{3+}$  and  $\text{Br}^-$   
 (c) It contains  $\text{Cs}^+$  and  $\text{Br}_3^-$   
 (d) It contains  $\text{Cs}^+$ ,  $\text{Br}^-$  and lattice  $\text{Br}_2$  molecule
39. Among  $\text{KO}_2$ ,  $\text{AlO}_2^-$ ,  $\text{BaO}_2$  and  $\text{NO}_2^+$ , unpaired electron is present in  
 (a)  $\text{KO}_2$  only (b)  $\text{NO}_2^+$  and  $\text{BaO}_2$   
 (c)  $\text{KO}_2$  and  $\text{AlO}_2^-$  (d)  $\text{BaO}_2$  only
40. In which case there is change in hybridisation when  
 (a)  $\text{NH}_3$  is protonated  
 (b)  $\text{AlH}_3$  combines with  $\text{H}^-$   
 (c) in both cases  
 (d) in none of the above case
41. Molecular shapes of  $\text{SF}_4$ ,  $\text{CF}_4$  and  $\text{XeF}_4$  are  
 (a) the same, with 2, 0 and 1 lone pair of electrons respectively  
 (b) the same, with 1, 1 and 1 lone pair of electrons respectively  
 (c) different with 0, 1 and 2 lone pair of electrons respectively  
 (d) different with 1, 0 and 2 lone pair of electrons respectively

42. The hybridisation of atomic orbitals of N in  $\text{NO}_2^+$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are respectively

- (a)  $sp$ ,  $sp^2$ ,  $sp^3$  (b)  $sp$ ,  $sp^3$ ,  $sp^2$   
(c)  $sp^2$ ,  $sp$ ,  $sp^3$  (d)  $sp^2$ ,  $sp^3$ ,  $sp$

43. Amongst  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$ , the one with the highest boiling point is

- (a)  $\text{H}_2\text{O}$  because of hydrogen bonding  
(b)  $\text{H}_2\text{Te}$  because of higher molecular weight  
(c)  $\text{H}_2\text{S}$  because of hydrogen bonding  
(d)  $\text{H}_2\text{Se}$  because of lower molecular weight

44. Which is paramagnetic and coloured?

- (a)  $\text{K}_2\text{Cr}_2\text{O}_7$  (b)  $(\text{NH}_4)_2[\text{TiCl}_6]$   
(c)  $\text{VOSO}_4$  (d)  $\text{K}_3[\text{Cu}(\text{CN})_4]$

45.  $\text{MgSO}_4$  is soluble while  $\text{BaSO}_4$  is insoluble in  $\text{H}_2\text{O}$ .

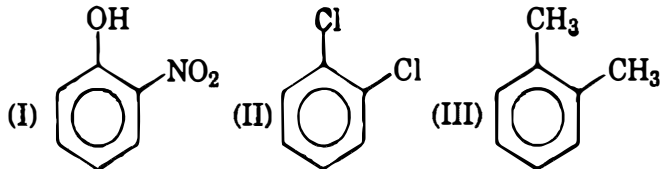
This is because

- (a) lattice energy of  $\text{BaSO}_4$  is greater than  $\text{MgSO}_4$   
(b)  $\text{BaSO}_4$  is more covalent than  $\text{MgSO}_4$   
(c) hydration energy of  $\text{Mg}^{2+}$  is greater than  $\text{Ba}^{2+}$   
(d) lattice energy of  $\text{MgSO}_4$  is greater than  $\text{BaSO}_4$

46. The strength of bonds by overlapping of atomic orbitals is in order

- (a)  $s-s > s-p > p-p$  (b)  $s-s < p-p < s-p$   
(c)  $s-p < s-s < p-p$  (d)  $p-p < s-s < s-p$

47. Correct order of dipole moment is



- (a)  $\text{I} = \text{II} = \text{III}$  (b)  $\text{I} < \text{II} < \text{III}$   
(c)  $\text{I} > \text{II} > \text{III}$  (d)  $\text{II} < \text{III} < \text{I}$

48. A : tetracyanomethane B : carbon dioxide

C : benzene

D : 1,3-butadiene

Ratio of  $\sigma$  and  $\pi$  bonds is in order

- (a)  $A = B < C < D$   
(b)  $A = B < D < C$   
(c)  $A = B = C = D$   
(d)  $C < D < A < B$

49. Which of the following molecules has the shortest nitrogen-to-carbon bond?

- (a)  $\text{C}_2\text{H}_4$  (b)  $\text{C}_2\text{H}_6$   
(c)  $\text{C}_2\text{H}_2$  (d)  $\text{C}_2\text{Cl}_6$

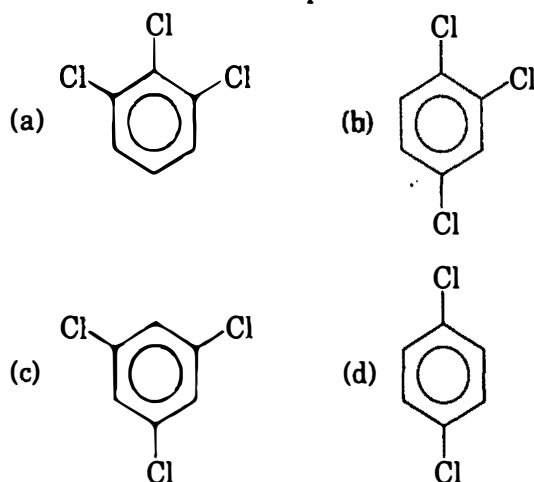
50. Which of the following species are isoelectronic?

- (a)  $\text{NH}_4^+$ ,  $\text{CH}_4$  (b)  $\text{N}_2$ ,  $\text{CO}$   
(c)  $\text{C}_6\text{H}_6$ ,  $\text{B}_3\text{N}_3\text{H}_6$  (d) All of these

51. Which of the following molecules does not have a dipole moment?

- (a)  $\text{IBr}$  (b)  $\text{CHCl}_3$   
(c)  $\text{CH}_2\text{Cl}_2$  (d)  $\text{BF}_3$

52. Which has maximum dipole moment?



53. Bond order of  $\text{O}_2$ ,  $\text{O}_2^+$ ,  $\text{O}_2^-$  and  $\text{O}_2^{2-}$  is in order

- (a)  $\text{O}_2^- < \text{O}_2^{2-} < \text{O}_2 < \text{O}_2^+$   
(b)  $\text{O}_2^{2-} < \text{O}_2^- < \text{O}_2 < \text{O}_2^+$   
(c)  $\text{O}_2^+ < \text{O}_2 < \text{O}_2^- < \text{O}_2^{2-}$   
(d)  $\text{O}_2 < \text{O}_2^+ < \text{O}_2^- < \text{O}_2^{2-}$

54. Central O atom in  $\text{O}_3$  is ..... hybridised.

- (a)  $sp$  (b)  $sp^2$   
(c)  $sp^3$  (d)  $dsp^2$

55. Which of the following species contain at least one atom that violates the octet rule?

- (a)  $\text{O}-\text{Cl}-\text{O}$  (b)  $\text{F}-\text{Xe}-\text{F}$   
(c) Both of these (d) None of these

56.  $\text{ZnCO}_3$  is thermally more stable than  $\text{MgCO}_3$ , because

- (a)  $\text{Mg}(\text{OH})_2$  exhibits only basic properties while  $\text{Zn}(\text{OH})_2$  is amphoteric  
(b) polarising action of  $\text{Zn}^{2+}$  with 18-electron configuration on the anion is larger than that of  $\text{Mg}^{2+}$  with a noble-gas electron configuration and of same size and charge.  
(c) both (a) and (b) are correct  
(d) none of the above is correct

57. Polarising action of  $\text{Cd}^{2+}$  on anions is stronger than that of  $\text{Ca}^{2+}$  because

- (a) the charges of the ions are same  
(b) their radii are same ( $\text{Ca}^{2+} = 0.104 \text{ nm}$ ;  $\text{Cd}^{2+} = 0.099 \text{ nm}$ )  
(c) the  $\text{Ca}^{2+}$  ion has a noble-gas electron configuration, and the  $\text{Cd}^{2+}$  ion, an 18-electron configuration of its outer shell  
(d) all of the above are correct

58. Which of the following is not stable?

- (a)  $\text{H}_2^+$  (b)  $\text{H}_2$   
(c)  $\text{He}_2$  (d)  $\text{HHe}$

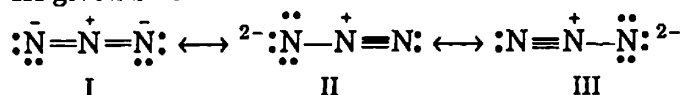
59. Which of the following has the smallest bond length?

- (a)  $\text{NO}^+$  (b)  $\text{NO}$   
(c)  $\text{NO}^-$  (d) Equal

60. Some of the following properties are important in determining whether an element has metallic properties

I : atomic number  
 II : atomic weight  
 III : number of valence electrons  
 IV : number of vacant atomic orbitals  
 V : total number of electronic shells in the atom  
 Select correct properties from the codes given below  
 (a) I, II, III, IV (b) I, III, IV, V  
 (c) III, IV (d) III, IV, V

61. Azide ion ( $\text{N}_3^-$ ) exhibits on N—N bond order of 2 and may be represented by resonance structures I, II and III given below



Select correct statements.

- (a) Structures I and II make greater contributions than III  
 (b) Structures II and III make greater contributions than I  
 (c) Structures I and III make greater contributions than II  
 (d) All the above three structures make equal contributions

62. Which of the following molecules are expected to exhibit intermolecular H-bonding?

I : Acetic acid II : *o*-nitrophenol  
 III : *m*-nitrophenol IV : *o*-boric acid

Select correct alternate.

- (a) I, II, III (b) I, II, IV  
 (c) I, III, IV (d) II, III, IV
63. In terms of polar character, which one of the following order is correct?
- (a)  $\text{NH}_3 < \text{H}_2\text{O} < \text{HF} < \text{H}_2\text{S}$   
 (b)  $\text{H}_2\text{S} < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$   
 (c)  $\text{H}_2\text{O} < \text{NH}_3 < \text{H}_2\text{S} < \text{HF}$   
 (d)  $\text{HF} < \text{H}_2\text{O} < \text{NH}_3 < \text{H}_2\text{S}$

64. How many  $\sigma$  and  $\pi$ -bonds are there in the molecule of tetracyano-ethylene?

(a)  $4\sigma, 14\pi$  (b)  $5\sigma, 13\pi$   
 (c)  $8\sigma, 10\pi$  (d)  $9\sigma, 9\pi$

65. Match List I with List II and select the correct answer

| List I (species) |                 |   |   | List II (O—N—O angle) |             |   |   |
|------------------|-----------------|---|---|-----------------------|-------------|---|---|
| A.               | $\text{NO}_2^+$ |   |   | 1.                    | $180^\circ$ |   |   |
| B.               | $\text{NO}_2$   |   |   | 2.                    | $132^\circ$ |   |   |
| C.               | $\text{NO}_2^-$ |   |   | 3.                    | $120^\circ$ |   |   |
| D.               | $\text{NO}_3^-$ |   |   | 4.                    | $115^\circ$ |   |   |
|                  |                 |   |   | 5.                    | $109^\circ$ |   |   |
| A                | B               | C | D | A                     | B           | C | D |
| (a) 5            | 4               | 3 | 2 | (b) 5                 | 2           | 4 | 3 |
| (c) 1            | 2               | 4 | 3 | (d) 1                 | 4           | 3 | 2 |

66. Metallic bonding is explained by  
 (a) band model (b) electron-sea model  
 (c) both (a) and (b) (d) None of these

67. Energy gaps between the highest filled band and the lowest empty bands in elements A, B, C and D are 0, 70, 530 and  $110 \text{ kJ mol}^{-1}$ . Thus

(a) element A is metal  
 (b) element C is insulator  
 (c) element B and D can be semiconductors  
 (d) all are correct conclusion about elements A, B, C and D

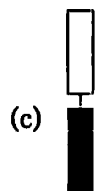
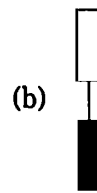
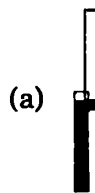
68. Select correct statements.

(a) The delocalised electrons in the  $\pi$ -orbitals of graphite cause this allotropic form to conduct electricity  
 (b) Pauling assigns "metallic valences" equal to their group number to the elements of IA to VIA  
 (c) Diatomic lithium molecules  $\text{Li}_2$  are stable towards dissociation  
 (d) All the above are correct statements

69. Solutions of alkali metals in liquid ammonia at  $-33^\circ\text{C}$  conduct electricity without chemical reaction at the electrodes. Hence, conductivity should

(a) increase as temperature is lowered  
 (b) decrease as temperature is lowered  
 (c) remain constant on changing the temperature  
 (d) there is always interaction of alkali metal with liquid ammonia

70. Which represents metallic character in an element?



(d) None of these

71. Isoelectronic species are

(a)  $\text{CO}, \text{CN}^-, \text{NO}^+, \text{N}_2, \text{BF}$   
 (b)  $-\text{CH}_3, -\ddot{\text{N}}\text{H}_2, -\ddot{\text{O}}\text{H}, -\ddot{\text{F}}:$   
 (c)  $>\text{CH}_2, >\ddot{\text{N}}\text{H}, >\ddot{\text{O}}:$   
 (d) all of the above

72. Select, isoelectronic species out of

$\text{CO}, >\text{CH}, >\text{N}: = \text{CH}_2, =\ddot{\text{O}}:, >\ddot{\text{O}}^{\oplus}, =\ddot{\text{N}}\text{H} >\ddot{\text{N}}\text{H}$   
 (a)  $>\text{CH} >\text{N}: >\ddot{\text{O}}^{\oplus}$  (b)  $=\text{CH}_2, =\ddot{\text{N}}\text{H}, =\ddot{\text{O}}:$   
 (c) both (a) and (b) (d) None of these

73. Some group in species in Column I are isoelectronic with that in II

| Column I                    | Column II                                                                               |
|-----------------------------|-----------------------------------------------------------------------------------------|
| HONO <sub>2</sub> , OCO, CO | (OH) <sub>2</sub> CO, F <sub>2</sub> CO, ONN, BF,<br>(CH <sub>3</sub> ) <sub>2</sub> CO |

Select isoelectronic groups in Column I to Column II

- | Column I                               | Column II                                                                   |
|----------------------------------------|-----------------------------------------------------------------------------|
| (a) (H <sub>2</sub> N) <sub>2</sub> CO | (HO) <sub>2</sub> CO, F <sub>2</sub> CO, (CH <sub>3</sub> ) <sub>2</sub> CO |
| (b) HONO <sub>2</sub>                  | CH <sub>3</sub> NO <sub>2</sub>                                             |
| (c) CO                                 | BF                                                                          |
| (d) all of the above                   |                                                                             |
74. Decreasing bond-order are expected to be
- |                                                                  |                                                                                                  |
|------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|
| (a) ClO <sub>4</sub> <sup>-</sup> > IO <sub>4</sub> <sup>-</sup> | (b) ClO <sub>3</sub> <sup>-</sup> > BrO <sub>3</sub> <sup>-</sup> > IO <sub>3</sub> <sup>-</sup> |
| (c) both (a) & (b)                                               | (d) None of these                                                                                |
75. Out of NO, NO<sup>+</sup>, O<sub>2</sub>, NO<sup>-</sup>, O<sub>2</sub><sup>+</sup> select species with same bond-order and paramagnetic.

**Electron Bond-order**

- |                             |    |     |              |
|-----------------------------|----|-----|--------------|
| (a) NO                      | 15 | 2.5 | Paramagnetic |
| O <sub>2</sub> <sup>+</sup> | 15 | 2.5 |              |
| (b) O <sub>2</sub>          | 16 | 2   | Paramagnetic |
| NO <sup>-</sup>             | 16 | 2   |              |
- (c) Both (a) and (b)  
(d) None of the above
76. Formation of anion from a neutral atom X is favoured by
- |                              |                            |
|------------------------------|----------------------------|
| (a) high electron affinity   | (b) large size of X        |
| (c) low ionisation potential | (d) high charge on anion X |
77. When a chemical bond is formed, there is decrease in
- |                     |                      |
|---------------------|----------------------|
| (a) kinetic energy  | (b) potential energy |
| (c) repulsive force | (d) attractive force |
78. Which of the following bonds is the weakest?
- |                           |                   |
|---------------------------|-------------------|
| (a) Coordinate bond       | (b) Hydrogen bond |
| (c) van der Waals' forces | (d) Covalent bond |
79. An ionic compound A<sup>+</sup>B<sup>-</sup> is most likely to be formed from A and B when
- |                                   |                                   |
|-----------------------------------|-----------------------------------|
| (a) ionisation energy of A is low | (b) electron affinity of B is low |
| (c) electronegativity of B is low | (d) ionisation energy of B is low |
80. In I<sub>3</sub><sup>-</sup>, Lewis base is
- |                                 |                                 |
|---------------------------------|---------------------------------|
| (a) I <sub>2</sub>              | (b) I <sup>-</sup>              |
| (c) I <sub>2</sub> <sup>+</sup> | (d) I <sub>2</sub> <sup>-</sup> |
81. Which set contains no ionic species?
- |                                                            |                                                          |
|------------------------------------------------------------|----------------------------------------------------------|
| (a) NH <sub>4</sub> Cl, OF <sub>2</sub> , H <sub>2</sub> S | (b) CO <sub>2</sub> , CCl <sub>4</sub> , Cl <sub>2</sub> |
| (c) BF <sub>3</sub> , AlF <sub>3</sub> , TiF <sub>3</sub>  | (d) I <sub>2</sub> , CaO, CH <sub>3</sub> Cl             |

82. Which combination will give the strongest ionic bond?

- |                                          |                                          |
|------------------------------------------|------------------------------------------|
| (a) K <sup>+</sup> and Cl <sup>-</sup>   | (b) K <sup>+</sup> and O <sup>2-</sup>   |
| (c) Ca <sup>2+</sup> and Cl <sup>-</sup> | (d) Ca <sup>2+</sup> and O <sup>2-</sup> |

83. Ionisation energies (IE) and electron affinities (EA) of F and Cl are given below:

| Element | IE      | EA      |
|---------|---------|---------|
| F       | 17.4 eV | 3.45 eV |
| Cl      | 13.0 eV | 3.61 eV |

Compound formed between F and Cl is predominantly

- |                                    |                                                                         |
|------------------------------------|-------------------------------------------------------------------------|
| (a) F <sup>+</sup> Cl <sup>-</sup> | (b) Cl <sup>+</sup> F <sup>-</sup>                                      |
| (c) F—Cl                           | (d) Cl $\begin{smallmatrix} \nearrow F \\ \searrow F \end{smallmatrix}$ |

84. Elements A, B and C have respectively 1, 3 and 5 electrons in valence shell. Ionic compound is not formed from

- |             |             |
|-------------|-------------|
| (a) A and C | (b) A and B |
| (c) B and B | (d) B and C |

85. Mg<sup>2+</sup>O<sup>2-</sup> is formed since

- |                      |                    |
|----------------------|--------------------|
| (a) IE of Mg is low  | (b) EA of O is low |
| (c) IE of Mg is high | (d) IE of O is low |

86. Solubility of KCl is maximum in

- |                                        |                                      |
|----------------------------------------|--------------------------------------|
| (a) CH <sub>3</sub> CH <sub>2</sub> OH | (b) CH <sub>3</sub> OCH <sub>3</sub> |
| (c) H <sub>2</sub> O                   | (d) CH <sub>3</sub> COOH             |

87. Which pair is not correct order of lattice energy?

- |                                           |                                           |
|-------------------------------------------|-------------------------------------------|
| (a) KCl > MgO                             | (b) AlN > MgO                             |
| (c) BeCO <sub>3</sub> > MgCO <sub>3</sub> | (d) BeCO <sub>3</sub> = MgCO <sub>3</sub> |

88. Solubility of NaCl, Na<sub>2</sub>SO<sub>4</sub> and Na<sub>3</sub>PO<sub>4</sub> in water in increasing order is

- |                                                                              |
|------------------------------------------------------------------------------|
| (a) NaCl < Na <sub>2</sub> SO <sub>4</sub> < Na <sub>3</sub> PO <sub>4</sub> |
| (b) Na <sub>3</sub> PO <sub>4</sub> < Na <sub>2</sub> SO <sub>4</sub> < NaCl |
| (c) NaCl < Na <sub>3</sub> PO <sub>4</sub> < Na <sub>2</sub> SO <sub>4</sub> |
| (d) Na <sub>2</sub> SO <sub>4</sub> < NaCl < Na <sub>3</sub> PO <sub>4</sub> |

89. Select correct statement.

- |                                                                                                                                                                                                                                                                |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| (a) LiF and MgO are isostructural and also isodimensional, but a crystal of MgO is much harder than one of LiF                                                                                                                                                 |
| (b) The thermal stability of the isomorphous sulphates of Ca <sup>2+</sup> , Sr <sup>2+</sup> and Ba <sup>2+</sup> w.r.t. decomposition into metal oxide and sulphur trioxide increases in the order CaSO <sub>4</sub> , SrSO <sub>4</sub> , BaSO <sub>4</sub> |
| (c) Both (a) & (b)                                                                                                                                                                                                                                             |
| (d) None of the above                                                                                                                                                                                                                                          |

90. Select correct statement.

- |                                                                                                                            |
|----------------------------------------------------------------------------------------------------------------------------|
| (a) Both lattice energy and hydration energies decrease with ionic size                                                    |
| (b) Lattice energy can be calculated using Born-Haber cycle                                                                |
| (c) If the anion is large compared to the cation, the lattice energy will remain almost constant within a particular group |
| (d) All the above are correct statements                                                                                   |

91. Which of the following compounds has both ionic and covalent bonding?  
 (a) NaBr (b) Ba(CN)<sub>2</sub>  
 (c) PCl<sub>5</sub> (d) CH<sub>3</sub>CH<sub>2</sub>OH
92. Compound X is highly volatile and insoluble in water. Bonding in X is  
 (a) ionic (b) covalent  
 (c) polar covalent (d) coordinate
93. The maximum covalency is equal to the number of  
 (a) paired *p*-electrons  
 (b) unpaired *s*-electrons  
 (c) unpaired *s*- and *p*-electrons  
 (d) *s*- and *p*-electrons in the valence shell
94. Select incorrect statement.  
 (a) Double bond is shorter than a single bond  
 (b)  $\sigma$ -bond is weaker than a  $\pi$ -bond  
 (c) Double bond is stronger than a single bond  
 (d) Covalent bond is stronger than a hydrogen bond
95. The As—Cl bond distance in AsCl<sub>3</sub> is 2.20 Å. If radius of chlorine atom is 0.99 Å then radius of As atom is  
 (a) 0.24 Å (b) 3.19 Å  
 (c) 1.21 Å (d) 2.09 Å
96. Covalency of carbon in the CO molecule is three because  
 (a) an unexcited carbon atom has two unpaired electrons  
 (b) the carbon atom can be an acceptor of an electron pair  
 (c) the carbon atom has four valence electrons  
 (d) maximum covalency of carbon is three
97. The number of electron dots in Lewis structure indicates  
 (a) number of valence electrons in an atom  
 (b) number of protons in the nucleus of the atom  
 (c) total number of electrons in an atom  
 (d) total number of electrons and protons in an atom
98. If there are five electron pairs in outer shell, then structure and bond angle as predicted by Sidgwick-Powell theory is  
 (a) octahedron, 90°  
 (b) trigonal bipyramidal, 120° and 90°  
 (c) pentagonal bipyramidal, 72° and 90°  
 (d) tetrahedron, 109° 28'
99. Octet rule is not followed in  
 (a) CCl<sub>4</sub>, N<sub>2</sub>O<sub>4</sub> and N<sub>2</sub>O<sub>5</sub> (b) BF<sub>3</sub>, BeCl<sub>2</sub> and NO<sub>2</sub>  
 (c) NaCl, MgCl<sub>2</sub>, MgO (d) PCl<sub>3</sub>, NH<sub>3</sub>, H<sub>2</sub>O
100. Which has maximum number of lone-pairs of electrons on the central atom?  
 (a) XeF<sub>2</sub> (b) H<sub>3</sub>O<sup>+</sup>  
 (c) XeF<sub>4</sub> (d) XeF<sub>6</sub>
101. Geometrical configuration of BF<sub>3</sub> and NF<sub>3</sub> molecules is  
 (a) the same because of same covalency of the central atom  
 (b) different because BF<sub>3</sub> is polar and NF<sub>3</sub> is non-polar  
 (c) different because BF<sub>3</sub> is non-polar and NF<sub>3</sub> is polar  
 (d) none of the above is correct
102. Coordinate covalent bond is absent in  
 (a) [Fe(CN)<sub>6</sub>]<sup>4-</sup>  
 (b) adduct of NH<sub>3</sub> and BH<sub>3</sub>  
 (c) H<sub>3</sub>O<sup>+</sup>  
 (d) PCl<sub>3</sub>
103. The compound NH<sub>3</sub>—BF<sub>3</sub> can be easily separated into its compounds because  
 (a) BF<sub>3</sub> is highly reactive  
 (b) NH<sub>3</sub> is highly reactive  
 (c) BF<sub>3</sub> and NH<sub>3</sub> are unstable  
 (d) BF<sub>3</sub> and NH<sub>3</sub> have their independent existence
104. Consider following compounds  
 I: K<sub>4</sub>[Fe(CN)<sub>6</sub>], II: NH<sub>4</sub>Cl, III: H<sub>2</sub>SO<sub>4</sub>  
 Ionic, covalent and coordinate bonds are present in  
 (a) I, II and III (b) I and III  
 (c) II and III (d) I and II
105. Which statement is not correct about NO<sub>2</sub>?  
 (a) It is paramagnetic  
 (b) It forms dimer and paramagnetism is lost  
 (c) It has one coordinate bonds  
 (d) It has nitrogen oxygen triple bond
106. In ammonia, H—N—H bond angle is  
 (a) 106.7° (b) 104.5°  
 (c) 109.5° (d) 120°
107. The angle between the bonding orbitals of a molecule AX<sub>3</sub> with zero dipole moment is  
 (a) 120° (b) 109°  
 (c) 104° (d) 180°
108. Number of bonding pairs (*X*) and lone pairs (*Y*) around the central atom in the I<sub>3</sub><sup>-</sup> ion are
- | <i>X</i> | <i>Y</i> | <i>X</i> | <i>Y</i> |
|----------|----------|----------|----------|
| (a) 2    | 2        | (b) 2    | 3        |
| (c) 3    | 2        | (d) 4    | 3        |
109. The nitrogen atoms in NH<sub>3</sub>, NH<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> are all surrounded by eight electrons. When these species are arranged in increasing order of H—N—H bond angle, correct order is  
 (a) NH<sub>3</sub>, NH<sub>2</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> (b) NH<sub>4</sub><sup>+</sup>, NH<sub>2</sub><sup>-</sup>, NH<sub>3</sub>  
 (c) NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, NH<sub>2</sub><sup>-</sup> (d) NH<sub>2</sub><sup>-</sup>, NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>
110. Which of these molecules have non-bonding electron pairs on the central atom?  
 I: SF<sub>4</sub>; II: ICl<sub>3</sub>; III: SO<sub>2</sub>  
 (a) II only (b) I and II only  
 (c) I and III only (d) I, II and III





131. The cyanide ion  $\text{CN}^-$  and the nitrogen molecule  $\text{N}_2$  are isoelectronic. However, in contrast to  $\text{CN}^-$ ,  $\text{N}_2$  is chemically inert due to
- unsymmetrical electron distribution
  - low bond energy
  - absence of bond polarity
  - presence of greater number of electrons in bonding

132. Select correct statement about carbonium ion  $\text{CH}_5^+$
- This cation shares eight electrons among five bonds
  - There is no empty orbital
  - It is not electron deficient
  - All the above are correct statements

133. Select correct statement about carbenium ion  $\text{CH}_3^+$
- It is planar with empty  $p$ -orbital
  - There are three sigma ( $\text{C}-\text{H}$ ) bonds
  - It is electron deficient with six electron in outer-shell
  - All the above are correct statements

134. Which of the following has maximum bond energy?

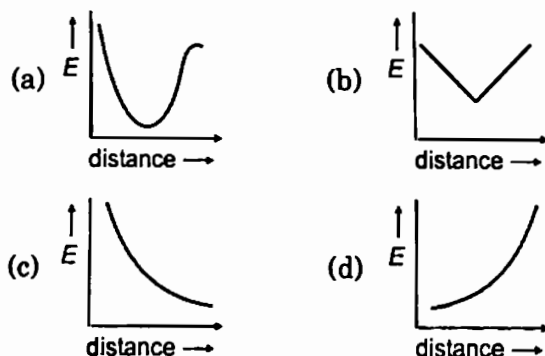
- $\text{O}_2^-$
- $\text{O}_2^+$
- $\text{O}_2$
- $\text{O}_2^{2-}$

135. In which pair or pairs is the stronger bond found in the first species?

I :  $\text{O}_2^-$ ,  $\text{O}_2$ ; II :  $\text{N}_2$ ,  $\text{N}_2^+$ ; III :  $\text{NO}^+$ ,  $\text{NO}^-$

- I only
- II only
- I and III only
- II and III only

136. Which plot best represents the potential energy ( $E$ ) of two hydrogen atoms as they approach one another to form a hydrogen molecule?



137. Number of unpaired electrons in  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$  is

- 2
- 3
- 4
- 5

138.  $dsp^2$  hybridisation is in

- $[\text{Ni}(\text{CN})_4]^{2-}$
- $[\text{Pt}(\text{en})_2]^{2+}$
- both (a) and (b)
- none of these

139. Select outer  $d$ -complexes

I :  $[\text{Fe}(\text{CN})_6]^{3-}$ ; II :  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

III :  $[\text{CoF}_6]^{3-}$

- II, III
- I, II
- I, III
- I, II, III

140. A set of inner  $d$ -complex is

- $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $[\text{Pt}(\text{en})_2]^{2+}$
- $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{CoF}_6]^{3-}$ ,  $[\text{Cr}(\text{CN})_6]^{3-}$
- both (a) and (b)
- none of the above

## One or More Than One Options Correct

1. Which of the following have identical bond-order?

- $\text{CN}^-$
- $\text{O}_2^-$
- $\text{NO}^+$
- $\text{CN}^+$

2. Select correct statement(s) about  $\text{C}_3^{4-}$  ion

- It reacts with  $\text{H}_2\text{O}$  forming  $\text{C}_3\text{H}_6$
- It reacts with  $\text{H}_2\text{O}$  forming  $\text{C}_3\text{H}_4$
- It has two sigma and two pi bonds
- It has three sigma and one pi bonds

3. The planar shape of  $\text{N}(\text{SiH}_3)_3$  is explained by the

- type of hybrid orbitals of nitrogen
- additional  $d\pi-p\pi$  overlap along the  $\text{N}-\text{Si}$  bond
- higher electronegativity of nitrogen
- higher electronegativity of silicon

4. Which are the species in which sulphur undergoes  $sp^3$  hybridisation?

- $\text{SF}_4$
- $\text{SCl}_2$
- $\text{SO}_4^{2-}$
- $\text{H}_2\text{S}$

5. Which of the following are non-polar?

- $\text{SiF}_4$
- $\text{XeF}_4$
- $\text{SF}_4$
- $\text{BF}_3$

6. In which of the following pairs, molecules/ions have similar shape?

- $\text{CO}_2$  and  $\text{H}_2\text{O}$
- $\text{BF}_3$  and  $(\text{CH}_3)_3\text{C}^+$
- $\text{CCl}_4$  and  $\text{PtCl}_4$
- $\text{NH}_3$  and  $\text{BF}_3$

7. In  $\text{BrF}_3$  molecule, the lone pairs occupy equatorial position to minimize

- lone pair-bond pair repulsion only
- bond pair-bond pair repulsion only
- lone pair-lone pair repulsion and lone pair-bond pair repulsion
- lone pair-lone pair repulsion only

8.  $\text{H}_2\text{O}$  is dipolar, whereas  $\text{BeF}_2$  is not. It is because

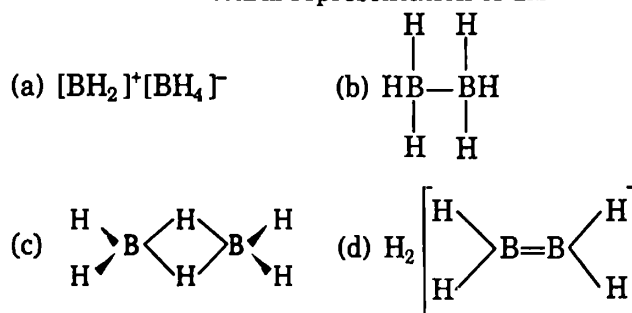
- the electronegativity of F is greater than that of O
- $\text{H}_2\text{O}$  involves hydrogen bonding whereas  $\text{BeF}_2$  is a discrete molecule
- $\text{H}_2\text{O}$  is linear and  $\text{BeF}_2$  is angular
- $\text{H}_2\text{O}$  is angular and  $\text{BeF}_2$  is linear

9. Among the following the pair in which the two species are not isostructural is

- $\text{SiF}_4$  and  $\text{SF}_4$
- $\text{IO}_3^-$  and  $\text{XeO}_3$
- $\text{BH}_4^-$  and  $\text{NH}_4^+$
- $\text{PF}_6^-$  and  $\text{SF}_6$

10.  $\text{PbCl}_4$  exists but  $\text{PbBr}_4$  and  $\text{PbI}_4$  do not because of  
 (a)  $\text{Br}^-$  and  $\text{I}^-$  ions are bigger in size  
 (b) chlorine is a gas  
 (c)  $\text{Br}_2$  and  $\text{I}_2$  are more electronegative  
 (d) inability of bromine and iodine to oxidise  $\text{Pb}^{2+}$  to  $\text{Pb}^{4+}$
11. Which is/are correct statements?  
 (a) A solute will dissolve in water if hydration energy is greater than lattice energy  
 (b) If the anion is large compared to the cation, the lattice energy will remain almost constant  
 (c) Solubility of II A hydroxide is in order.  
 $\text{Be(OH)}_2 < \text{Mg(OH)}_2 < \text{Ca(OH)}_2 < \text{Sr(OH)}_2$   
 (d) None of the above is correct
12. In which molecule is the van der Waals' force likely to be most important in determining melting point and boiling point?  
 (a)  $\text{ICl}$  (b)  $\text{Br}_2$   
 (c)  $\text{H}_2\text{S}$  (d)  $\text{CO}$
13. Which have linear structure?  
 (a)  $\text{BeF}_2$  (b)  $\text{Ag}[\text{CN}]_2^-$   
 (c)  $\text{CO}_2$  (d)  $\text{XeF}_2$
14. In  $\text{I}_3^-$   
 (a)  $\text{I}_2$  is Lewis acid and  $\text{I}^-$  as Lewis base  
 (b)  $\text{I}_2$  is Lewis base and  $\text{I}^-$  as Lewis acid  
 (c)  $\text{I}_3^-$  itself behaves as amphoteric anion  
 (d)  $\text{I}_3^-$  does not exist
15. In the following case (s), hybridisation of the underlined atom is affected  
 (a)  $\underline{\text{P}}\text{Cl}_5$  (solid) dissociates into  $\text{PCl}_4^+$  and  $\text{PCl}_6^-$   
 (b)  $\text{LiH}$  reacts with  $\underline{\text{Al}}\text{H}_3$  forming  $\text{LiAlH}_4$   
 (c)  $\underline{\text{N}}\text{H}_3$  is protonated  
 (d)  $\text{H}_3\underline{\text{P}}\text{O}_2$  is heated forming  $\text{PH}_3$  and  $\text{H}_3\text{PO}_3$
16. The correct order of the O—O bond length in  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  is  
 (a)  $\text{H}_2\text{O}_2 > \text{O}_3 > \text{O}_2$   
 (b)  $\text{O}_2 > \text{O}_3 > \text{H}_2\text{O}_2$   
 (c)  $\text{O}_2 > \text{H}_2\text{O}_2 > \text{O}_3$   
 (d)  $\text{O}_3 > \text{H}_2\text{O}_2 > \text{O}_2$
17. Which combinations of the compounds and their geometry are correct?  
 (a)  $\text{HgCl}_2$ —linear (b)  $\text{ClF}_3$ —V-shaped  
 (c)  $\text{ClF}_3$ —T-shaped (d)  $\text{ICl}_4^-$ —square planar
18. Which combination of the compounds with their magnetic moments are correct?  
 (a)  $\text{K}_3\text{Mn}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$   $\mu = 4.90 \text{ BM}$   
 (b)  $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$   $\mu = 5.92 \text{ BM}$   
 (c)  $\text{Ni}(\text{CO})_4$   $\mu = 0.00 \text{ BM}$   
 (d)  $[\text{Ni}(\text{CN})_4]^{2-}$   $\mu = 0.00 \text{ BM}$

19. The correct structural representation of diborane is



20. Which of the following is/are electron deficient compounds?  
 (a)  $\text{NaBH}_4$   
 (b)  $\text{B}_2\text{H}_6$   
 (c)  $\text{AlCl}_3$   
 (d)  $\text{C}_3^{4-}$

## Passage Comprehension Questions

### Passage 1

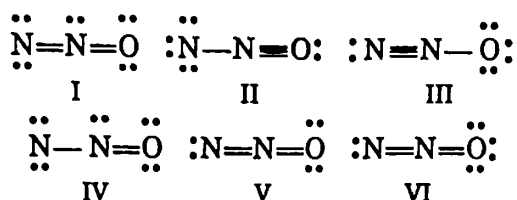
A paper published in the research journal *Science* in 2007 (S. Vallina and R. Simo, *Science*, 305, 506 Jan 26, 2007) reported studies of dimethyl sulphide (DMS, an important green house gas that is released by marine phytoplankton. This gas “represents the largest natural source of atmosphere sulphur and a major precursor of hygroscopic (*i.e.*, cloud forming) particles in clean air over the remote oceans, thereby acting to reduce the amount of solar radiation that crosses the atmosphere and is absorbed by ocean.”

Answer the following questions

- Steric number of sulphur in DMS is  
 (a) 2 (b) 3  
 (c) 4 (d) 5
- Select correct statement(s).  
 (a) Bond pair-bond pair repulsions of the two ( $\text{S}-\text{CH}_3$ ) bonds in DMS would be greater than the bond-pair bond-pair repulsions of the  $\text{S}-\text{CH}_3$  and  $\text{S}-\text{H}$  bonds in thiol.  
 (b) Bond angle  $\angle \text{C}-\text{S}-\text{C}$  in DMS is greater than bond angle  $\angle \text{C}-\text{S}-\text{H}$  in thiol  
 (c) Both (a) & (b) are correct  
 (d) None of the above is correct
- The mean sea water concentration of DMS in the ocean is 2.7 nM (nanomolar). How many molecules of DMS are present in  $1.0 \text{ m}^3$  of sea water?  
 (a)  $16.254 \times 10^{17}$  molecules  
 (b)  $2.7 \times 10^{17}$  molecules  
 (c)  $2.7 \times 10^{-6}$  molecules  
 (d)  $16.257 \times 10^9$  molecules

### Passage 2

Assume following structure of  $N_2O$  and answer the questions.



- Which is most favourable structure?  
(a) I (b) III  
(c) V (d) VI
- Select correct statement(s).  
(a) Structure I is not acceptable as there are 10 electron on N atom and 18 electrons total  
(b) Structure IV is not acceptable as there are only three bonds  
(c) Structure VI is not acceptable as there are 10 electrons on oxygen atom  
(d) All the above are correct statements
- Structure III is represented as  
(a)  $:\ddot{N} \equiv \ddot{N} - \ddot{O}^-$  (b)  $:\ddot{N} \equiv \ddot{N} - \ddot{O}^+$   
(c)  $:\ddot{N} = \ddot{N} - \ddot{O}^-$  (d)  $:\ddot{N} \equiv \ddot{N} - \ddot{O}^+$

### Passage 3

We consider dissociation energy of different species.

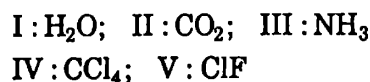
| Species | Dissociation energy<br>(kJ mol <sup>-1</sup> ) |
|---------|------------------------------------------------|
| $O_2^+$ | 642.9                                          |
| $O_2$   | 493.6                                          |
| $O_2^-$ | 395.0                                          |
| $N_2^+$ | 840.7                                          |
| $N_2$   | 941.7                                          |
| $N_2^-$ | 765.0                                          |
| $NO^+$  | 1046.9                                         |
| $NO$    | 026.9                                          |
| $NO^-$  | 487.8                                          |

Answer the following questions :

- In which case bond-order increases?  
(a)  $O_2$  changes to  $O_2^+$  (b)  $N_2$  changes to  $N_2^+$   
(c)  $NO$  changes to  $NO^-$  (d) In all cases
- In which case electron from anti-bonding MO (HOMO) is removed? (HOMO : Highest Occupied Molecular Orbital)  
(a)  $O_2$  to  $O_2^+$  (b)  $N_2$  to  $N_2^+$   
(c)  $N_2$  to  $N_2^-$  (d) In all cases
- In which case electron from bonding MO is removed?  
(a)  $O_2$  to  $O_2^+$  (b)  $N_2$  to  $N_2^+$   
(c)  $NO$  to  $NO^+$  (d)  $O_2$  to  $O_2^-$

### Passage 4

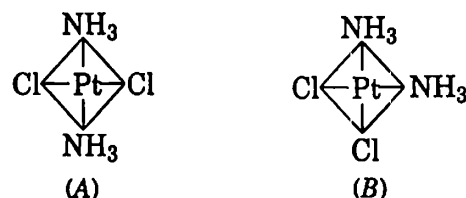
Consider the following molecules and answer the questions given :



- In which compound are the bonds most polar?  
(a)  $H_2O$  (b)  $CO_2$   
(c)  $CCl_4$  (d)  $ClF$
- Which compounds are not polar?  
(a)  $H_2O, CO_2$  (b)  $CO_2, NH_3$   
(c)  $H_2O, CCl_4$  (d)  $CO_2, CCl_4$
- Which atoms in  $H_2O$  and  $ClF$  are negatively charged?  
(a) O in  $H_2O$  and Cl in  $ClF$   
(b) H in  $H_2O$  and F in  $ClF$   
(c) O in  $H_2O$  and F in  $ClF$   
(d) None of the above is correct

### Passage 5

The platinum-chlorine distance has been found to be 2.32 Å in several crystalline compounds. This value applies to both of the compounds shown in figure,



Based on the above structures, answer the following questions

- Cl—Cl distance in structure (A) is  
(a) 2.32 Å (b) 4.64 Å  
(c) 1.16 Å (d) 9.28 Å
- Cl—Cl distance in structure (B) is  
(a) 2.32 Å (b) 1.52 Å  
(c) 2.15 Å (d) 3.28 Å
- A is  
(a) *cis*-isomer (b) *trans*-isomer  
(c) chiral isomer (d) none of these
- B is  
(a) *cis*-isomer (b) nuclear isomer  
(c) chiral isomer (d) coordinate isomer

### Passage 6

By the following method you can predict the geometrical shape of species with only one central atom, without first drawing the Lewis structure:

- Total number of electron pairs  
= (number of valence electrons  $\pm$  electrons (for ionic charge)/2

2. Number of bond electron pairs = number of atoms - 1
3. Number of electron pairs around central atom = total number of electron pairs - 3 [number terminal atoms (except H)]
4. Number of lone pair = (number of central electron pairs - number bond pairs)

Read the above method and answer the following questions:

1. If A is the central element of the molecule containing A and X element and E the number of electron pairs round it then VSEPR notation  $AX_3E$  will be for the molecules

- (a)  $PCl_5, ICl_4^-$  (b)  $NH_3, H_2O$   
(c)  $NH_3, ClO_3^-$  (d)  $ICl_4^-, ClO_3^-$

2. VSEPR notation of  $PCl_5, H_2O$  and  $ICl_4^-$  are

- |     | $PCl_5$ | $H_2O$    | $ICl_4^-$ |
|-----|---------|-----------|-----------|
| (a) | $AX_5$  | $AX_2E_2$ | $AX_4E_2$ |
| (b) | $AX_5$  | $AX_2E$   | $AX_4E$   |
| (c) | $AX_5$  | $AX_2$    | $AX_4E$   |
| (d) | $AX_5$  | $AX_2E_2$ | $AX_4E$   |

3. Square planar structure is predicted for

- (a)  $ICl_4^-, ClO_3^-$   
(b)  $PCl_4^+, PCl_6^-$   
(c)  $ICl_4^-, PCl_4^+$   
(d)  $ICl_4^-, [Ni(CN)_4]^{2-}$

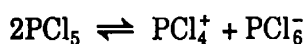
4. Based on above method, structure of the some of the molecules have been matched. Which is the incorrect matching?

- (a)  $PCl_5$  — trigonal bipyramidal  
(b)  $ClO_3^-$  — square planar  
(c)  $ICl_4^-$  — square planar  
(d)  $PCl_4^+$  — tetrahedral

### Passage 7

Read the following short write-up and answer the questions at the end of it.

In certain polar solvents  $PCl_5$  undergoes an ionisation reaction in which  $Cl^-$  ion leaves one  $PCl_5$  molecule and attaches itself to another.



1. Select **incorrect** statement(s).

- (a) Dissociation is a redox reaction  
(b) Hybridisation changes from  $sp^3d$  to  $sp^3d^2$  ( $PCl_6^-$ ) and  $sp^3$  ( $PCl_4^+$ )  
(c) Structure changes from trigonal bipyramidal to tetrahedral ( $PCl_4^+$ ) and octahedral ( $PCl_6^-$ )  
(d) None of the above is incorrect

2. Number of lone pairs around phosphorus in  $PCl_5, PCl_4^+$  and  $PCl_6^-$  are respectively

- (a) 0, 1, 2 (b) 0, 0, 0  
(c) 1, 2, 3 (d) 0, 2, 1

### Passage 8

Read the following short write-up and answer the questions at the end of it.

"Each of the following compounds has a nitrogen-nitrogen bond"

- (A)  $N_2$ , (B)  $N_2H_4$   
(C)  $N_2F_2$

Molecules may be polar or non-polar, that is dependent on the electronegativity difference between two atoms. Their bond-lengths (between N-atoms) have been 1.45 Å, 1.10 Å and 1.22 Å but not in correct order.

1. Compounds have been matched with their bond-length (between N-atoms). Which is not the correct matching?

- (a) A — 1.10 Å (b) B — 1.45 Å  
(c) C — 1.22 Å (d) None of these

2. Select incorrect statement(s).

- (a)  $N_2$  is an inert gas  
(b)  $N_2F_2$  has  $sp^2$ -hybridised N-atom  
(c)  $N_2H_4$  is an inert solvent  
(d)  $N_2H_4$  is used as rocket fuel

### Passage 9

Read the following short write up and answer the questions at the end of it.

Two substances having the same molecular formula,  $C_4H_8O$ , were examined in the gaseous state by electron diffraction. The carbon-oxygen distance was found to be 143 pm in the compound A and 124 pm in compound B.

C—O bond length = 143 pm

C=O bond length = 123 pm

1. Which of the above compounds is inert?

- (a) A (b) B  
(c) Both (a) and (b) (d) None of these

2. Which of the above can show functional isomerism?

- (a) A (b) B  
(c) Both (a) and (b) (d) None of these

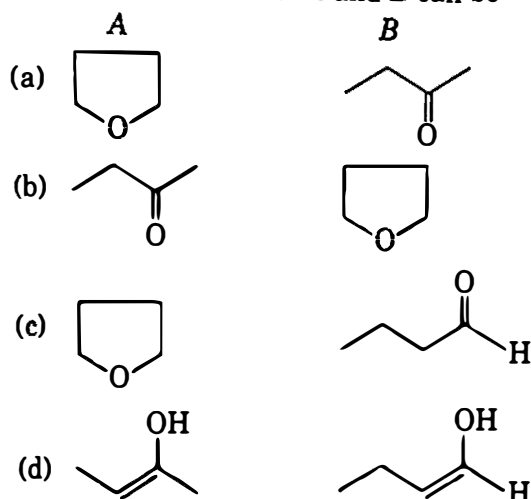
3. Keto-enol tautomerism occurs in

- (a) A (b) B  
(c) both (a) and (b) (d) none of these

4. Distinction between two functional isomers of the same main functional group can be made by

- (a) Iodoform test (b) Tollen's test  
(c)  $Br_2$  water (d) Phthalein test

5. Probable structures of A and B can be



### Passage 10

Read the following experimental fact and answer the question at the end of it.

A sample of lead (II) bromide,  $\text{PbBr}_2$ , was placed in a crucible. The ends of two carbon electrodes were put in the solid and connected to a lamp and power pack. At first the lamp did not light, but when the bromide was heated and began to melt the lamp began to glow.

- Select correct statement(s).
  - $\text{PbBr}_2$  is non-conducting in solid state
  - $\text{PbBr}_2$  is conducting in aqueous solution
  - $\text{PbBr}_2$  is conducting in fused state
  - $\text{PbBr}_2$  is non-conducting in molten state

### Passage 11

Read the following short-write up and answer the questions at the end of it.

"Methyl isocyanate is used to make certain pesticides. In December 1984, water leaked into a tank containing this substance at a chemical plant, producing a toxic cloud that killed thousands of people in Bhopal.

- Which is not the resonance structure of methyl isocyanate?
  - $\text{CH}_3-\ddot{\text{N}}=\text{C}=\ddot{\text{O}}:$
  - $\text{CH}_3-\ddot{\text{N}}^{\ominus}-\text{C}^{\oplus}=\ddot{\text{O}}:$
  - $\text{CH}_3-\text{N}=\ddot{\text{C}}-\ddot{\text{O}}^{\ominus}$
  - $\text{CH}_3-\text{N}^{\oplus}\equiv\text{C}-\ddot{\text{O}}^{\ominus}$
- Which of the atoms in  $\text{CH}_3\text{NCO}$  has maximum s-character?
  - N
  - O
  - C(in  $\text{CH}_3$ )
  - C(bonded to O and N)
- Total number of lone pairs are
  - 2
  - 3
  - 4
  - 5

### Assertion & Reason

Codes :

- Both A and R are true and R is the correct explanation of A.
- Both A and R are true but R is not the correct explanation of A.
- A is true but R is false.
- A is false but R is true.

1. **Assertion (A)** : On cooling, the brown colour of nitrogen dioxide disappears.

**Reason (R)** : On cooling  $\text{NO}_2$  undergoes dimerisation resulting in the pairing of odd electrons of  $\text{NO}_2$ .

2. **Assertion (A)** : Tin (Sn) exhibits +2 and +4 oxidation states only and not +3 oxidation state.

**Reason (R)** : Inert pair effect of electron pair in s-orbital is responsible.

3. **Assertion (A)** :  $\text{PbCl}_2$  is more stable than  $\text{PbCl}_4$ .

**Reason (R)** :  $\text{PbCl}_4$  is powerful oxidising agent.

4. **Assertion (A)** :  $\text{BF}_3$  is a weaker Lewis acid than  $\text{BCl}_3$ .

**Reason (R)** : The planar  $\text{BF}_3$  molecule is stabilised to a greater extent than  $\text{BCl}_3$  by B—X  $\pi$ -bonding.

5. **Assertion (A)** :  $\text{O}_2$  is paramagnetic in nature.

**Reason (R)** : Bond-order of oxygen is two.

6. **Assertion (A)** :  $\text{KO}_2$  is paramagnetic.

**Reason (R)** :  $\text{K}^+$  ion has unpaired electron.

7. **Assertion (A)** : Dipole moment of o-dichloro benzene is larger than the theoretical value.

**Reason (R)** : Due to dipole-dipole repulsion of two Cl-atoms in ortho position bond angle is greater than  $60^\circ$ .

8. **Assertion (A)** : N-atom in  $\text{NH}_3$  is  $sp^3$  hybridised and bond angle is  $107^\circ$ .

**Reason (R)** : lp-bp repulsion (VSEPR) decreases bond angle to  $107^\circ$ .

9. **Assertion (A)** :  $\text{P}_4$  exists but  $\text{N}_4$  does not exist.

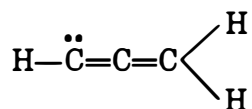
**Reason (R)** : In  $\text{P}_4$  form P-atoms are joined by single bonds while in  $\text{N}_4$ , two N-atoms are joined by double and other two by single bonds.

10. **Assertion (A)** :  $\text{PCl}_5$  exists but  $\text{NCl}_5$  does not exist.

**Reason (R)** : d-orbital in P-atom takes part in chemical bonding; this lacks in N-atom.

11. **Assertion (A)** : The C—C bond distance in methyl acetylene is unusually short (145 pm) for a single bond.

**Reason (R) :** Hyperconjugation involving “no bond” structure,

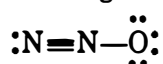


increases the bond order of the C — CH<sub>3</sub> bond.

**12. Assertion (A) :** Bond angle in NH<sub>3</sub> is greater than that in PH<sub>3</sub>.

**Reason (R) :** P—H bonds are longer and the lower electronegativity of P permits electron density to be displaced towards H to a greater extent than in the case of NH<sub>3</sub>.

**13. Assertion (A) :** Following structure is acceptable



**Reason (R) :** Octet rule is followed for each atom central N has positive charge and oxygen has negative charge.

## True & False

1. Solid sodium chloride does not conduct electricity.
2. Dipole moment of HF is less than that of HCl because of shorter bond length of HF.
3. Bond energy of all the P—Cl bonds in PCl<sub>3</sub> and PCl<sub>5</sub> is same.
4. The covalent molecule BeCl<sub>2</sub> has permanent dipole moment.
5. The H—N—H bond angle in NH<sub>3</sub> is greater than the H—As—H bond angle in AsH<sub>3</sub>.
6. All the molecules with polar bonds have dipole moment.
7. Sugden introduced singlet linkage in which one electron is donated instead of one pair of electrons.
8. PCl<sub>5</sub> in solid state dissociates into PCl<sub>4</sub><sup>+</sup> and PCl<sub>6</sub><sup>-</sup>.
9. O<sub>2</sub>, O<sub>2</sub><sup>-</sup> and O<sub>2</sub><sup>2-</sup> are paramagnetic species.
10. Dipole moment of BH<sub>3</sub> is zero.
11. Dipole moment of CHCl<sub>3</sub> is larger than that of HCl.
12. All the B—H bonds in B<sub>2</sub>H<sub>6</sub> are equivalent.
13. Hybridisation of sulphur in SO<sub>2</sub> is sp.
14. Bond length of (C=O) bond is larger than (C—O) bond in CO<sub>3</sub><sup>2-</sup>.
15. The highest occupied energy band is called the valence band and the lowest unoccupied energy band is called the conduction band.
16. NaCl conducts electricity only in aqueous solution.
17. C<sub>2</sub> and C<sub>3</sub> atoms in CH≡C—CH=CH<sub>2</sub> are respectively sp and sp<sup>2</sup> hybridised.

**18.** Structures of [Ni(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> and [Ni(CN)<sub>4</sub>]<sup>2-</sup> are different.

**19.** Dipole moment of [Ni(CN)<sub>4</sub>]<sup>2-</sup> is zero.

**20.** Dipole moment of o-dichloro benzene is smaller than the theoretical value, while in case of o-nitrophenol, value is larger than the theoretical value.

## Fill in the Blanks

1. The complex ion [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> has a ..... structure.
2. AlCl<sub>3</sub> is covalent while AlF<sub>3</sub> is ionic. The above fact can be justified on the basis of .....
3. Water has maximum density at ..... °C.
4. O<sub>2</sub> is ..... in nature because it has two unpaired electrons.
5. The abnormally large specific heat of water molecule can be explained on the basis of .....
6. The bond formed between two atoms one of low ionisation potential and the other of high electron affinity is .....
7. By the axial overlapping of two p-orbitals of same energy, a strong ..... bond is formed.
8. When NH<sub>3</sub> and BF<sub>3</sub> are bonded, NH<sub>3</sub> is a ..... and BF<sub>3</sub> is a .....
9. Types of bonding in NH<sub>4</sub>Cl are ..... and .....
10. NO<sub>2</sub> is ..... but N<sub>2</sub>O<sub>4</sub> is .....
11. Bond orders of oxygen, superoxide ion and peroxide ion are ..... and ..... and of these ..... and ..... are paramagnetic.
12. Hybridisation of N atom in NO<sub>2</sub>, NO<sub>3</sub><sup>-</sup> and NH<sub>3</sub> are respectively ..... and .....
13. Ni atom in [Ni(CN)<sub>4</sub>]<sup>2-</sup> is ..... hybridised and in Ni(CO)<sub>4</sub> is ..... hybridised.
14. Magnetic moment of iron in [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> is .....
15. A molecule like H—X is 50% ionic if electronegativity difference of H and X is ..... eV.
16. Out of NH<sub>3</sub>, PH<sub>3</sub> and AsH<sub>3</sub> boiling point of ..... is maximum and that of ..... is minimum.
17. Coordination number of H<sub>2</sub>O in liquid state is .....
18. When N<sub>2</sub> changes to N<sub>2</sub><sup>+</sup>, the N—N bond distance ..... and bond order.....
19. When O<sub>2</sub> changes to O<sub>2</sub><sup>-</sup> the O—O bond distance ..... and bond order .....
20. CN<sup>-</sup> and N<sub>2</sub> are isoelectronic. But in contrast to CN<sup>-</sup>, N<sub>2</sub> is chemically inert because of .....

21. Unsymmetrical  $\text{PCl}_5(\text{s})$  splits into ..... and .....
22. In  $\text{I}_3^-$ ,  $\text{I}_2$  is a ..... and  $\text{I}^-$  is a .....
23. Metallic bonding is explained by ..... and .....
24. In the case of insulators, the energy gap is ..... while in case of semiconductors energy gap is .....
25. The highest occupied energy band is called the ..... and lowest unoccupied energy band is called the .....

## Matrix-Match Type Questions

### I. Only One Correct

1. Match the compounds (in List I) with the structure (in List II)

| List I            | List II                 |
|-------------------|-------------------------|
| A. $\text{XeF}_4$ | 1. Distorted octahedral |
| B. $\text{XeF}_6$ | 2. Tetrahedral          |
| C. $\text{XeO}_3$ | 3. Square planar        |
| D. $\text{XeO}_4$ | 4. Pyramidal            |

2. Match the type of species (in List I) with the compound (in List II).

| List I                                           | List II            |
|--------------------------------------------------|--------------------|
| A. Ionic species                                 | 1. $\text{HCl}$    |
| B. Non-polar covalent                            | 2. $\text{LiCH}_3$ |
| C. Polar covalent species having sigma bond only | 3. $\text{KCH}_3$  |
|                                                  | 4. $\text{NO}$     |

3. Match the compounds (in List I) with the type of hybridisation on the central atom/ion (in List II).

| List I                                      | List II      |
|---------------------------------------------|--------------|
| A. $\text{BCl}_3$                           | 1. $sp^3$    |
| B. $\text{NH}_3$                            | 2. $sp^3d^2$ |
| C. $[\text{Cu}(\text{NH}_3)_4]^{2+}$        | 3. $sp^2$    |
| D. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ | 4. $dsp^2$   |

4. Match the compounds (in List I) with the structures (in List II).

| List I                       | List II               |
|------------------------------|-----------------------|
| A. $(\text{CH}_3)_3\text{B}$ | 1. Square planar      |
| B. $\text{NH}_4\text{Cl}$    | 2. Trigonal bipyramid |
| C. $[\text{ICl}_4]^-$        | 3. Tetrahedral        |
| D. $\text{PCl}_5$            | 4. Trigonal           |

5. Match type of bond (given in List I) with method of formation (given in List II).

| List I            | List II                  |
|-------------------|--------------------------|
| A. $\sigma$ -bond | 1. Lateral overlapping   |
| B. Covalent bond  | 2. Sharing of electrons  |
| C. Ionic bond     | 3. Transfer of electrons |
| D. $\pi$ -bond    | 4. Donating an electron  |
|                   | 5. Accepting an electron |
|                   | 6. Axial overlapping     |

6. Match the hybridization (in List I) with the respective geometrical shape of the hybrid orbitals (in List II).

| List I       | List II          |
|--------------|------------------|
| A. $sp$      | 1. Tetrahedral   |
| B. $sp^2$    | 2. Linear        |
| C. $sp^3$    | 3. Trigonal      |
| D. $dsp^2$   | 4. Square planar |
| E. $d^2sp^3$ | 5. Pyramidal     |
|              | 6. Octahedral    |

7. Match the list of type of bonds (List I) with list of compounds (List II).

| List I                 | List II                   |
|------------------------|---------------------------|
| A. Ionic               | 1. $\text{H}_2\text{O}$   |
| B. Single covalent     | 2. $\text{NH}_3$          |
| C. Coordinate covalent | 3. $\text{CaCl}_2$        |
| D. Hydrogen bond       | 4. $\text{C}_2\text{H}_2$ |
| E. Multiple covalent   | 5. $\text{CH}_4$          |
|                        | 6. $\text{NH}_4^+$        |

8. Match the species (in List I) with the bond order (in List II).

| List I            | List II |
|-------------------|---------|
| A. $\text{N}_2$   | 1. 1.0  |
| B. $\text{O}_2$   | 2. 2.0  |
| C. $\text{F}_2$   | 3. 2.5  |
| D. $\text{O}_2^+$ | 4. 3.0  |

9. Match the items under List (I) with items under List (II).

| List (I) Molecule       | List (II) Shape         |
|-------------------------|-------------------------|
| A. $\text{PCl}_5$       | 1. V-shaped             |
| B. $\text{F}_2\text{O}$ | 2. Trigonal planar      |
| C. $\text{BCl}_3$       | 3. Trigonal bipyramidal |
| D. $\text{NH}_3$        | 4. Trigonal pyramidal   |
|                         | 5. Tetrahedral          |

10. Match List I (Hybrid bond orbitals) with List II in (species) and select the correct answer.

| List I       | List II            |
|--------------|--------------------|
| A. $sp^3$    | 1. $ICl_4^-$       |
| B. $dsp^2$   | 2. $TeCl_4$        |
| C. $sp^3d$   | 3. $MnO_4^-$       |
| D. $sp^3d^2$ | 4. $Ni(CN)_4^{2-}$ |

11. Match the species (in List I) with bond-order (in List II) and number of unpaired electrons (in List III).

| List I<br>(Species) | List II<br>(Bond-order) | List III<br>(Unpaired electron) |
|---------------------|-------------------------|---------------------------------|
| $Be_2^+$            | 2                       | 2                               |
| $O_2$               | 2.5                     | 0                               |
| $O_2^+$             | 0.5                     | 1                               |
| $O_2^{2-}$          | 1.0                     | 1                               |

12. Match the species (in List I) with Bond-order (in List II) and isoelectronic species (in List III).

| List I<br>(Species) | List II<br>(Bond-order) | List III<br>(Isoelectronic species) |
|---------------------|-------------------------|-------------------------------------|
| $NO^+$              | 2.5                     | $O_2^+$                             |
| $NO$                | 3.0                     | $O_2$                               |
| $NO^-$              | 2.0                     | $N_2$                               |

## II. One or More Correct

1. Match the species in Column I with corresponding character(s) in Column II.

| Column I    | Column II              |
|-------------|------------------------|
| A. $CH_3^+$ | 1. Bond order 3        |
| B. $CH_5^+$ | 2. Paramagnetic        |
| C. $NO^+$   | 3. $sp^2$              |
| D. $O_2$    | 4. Carbocation         |
| E. $N_2$    | 5. Carbonium ion       |
|             | 6. Octet rule violated |

2. Match the species in Column I with the corresponding character(s) in Column II.

| Column I     | Column II                |
|--------------|--------------------------|
| A. $CO_2$    | 1. Zero dipole moment    |
| B. $CH_4$    | 2. Expansion of octet    |
| C. $ClF_2^+$ | 3. $sp^3$ hybridisation  |
| D. $PCl_5$   | 4. $sp^3d$ hybridisation |
| E. $ClF_2^-$ | 5. Linear                |

## Integer Answer Types

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the ORS have to be darkened. For example, if the correct answers to question number X, Y, Z and W (say) are 6, 0, 9 and 2, respectively

| X | Y | Z |
|---|---|---|
| ① | ① | ① |
| ② | ② | ② |
| ③ | ③ | ③ |
| ④ | ④ | ④ |
| ⑤ | ⑤ | ⑤ |
| ⑥ | ⑥ | ⑥ |
| ⑦ | ⑦ | ⑦ |
| ⑧ | ⑧ | ⑧ |
| ⑨ | ⑨ | ⑨ |

### Set I

- Steric number of  $CH_4$  is .....
- Steric number of  $H_2O$  is .....
- Lone pairs in  $I_3^-$  are .....
- Bond-order in  $NO^+$  is .....
- Number of hybrid orbitals in  $XeF_4$  is .....
- Number of unpaired electron(s) in  $O_2^-$  is/are .....
- Formal charge on sulphur in  $SO_2$  is .....
- In a compound of Xe, F and O  
Xe = 60.4% (131.3)  
F = 17.5% (19.0)  
Thus, number of oxygen atom .....

### Set II

This section contains 9 questions.

- A slightly polar molecule  $AB$  has dipole moment 0.24 D. If bond-length is 1 Å, ionic character is .....
- In a very ideal imaginary condition, a sample of was taken, and its osmotic pressure was found to 0.274 atm at 300 K. (density = 1 g/mL). Thus, number of water units attached to one water unit is .....
- In  $O_3$ , central oxygen atom is hypervalent. It shares ..... electron pairs.
- Total number of orbitals involved in the formation of hybrid orbitals in  $ClF_2^-$  is .....
- Total number of orbitals involved in the formation of hybrid orbitals in  $ClF_2^+$  is .....
- $AX_4$  forms square planar type structure. Distance between A and X atoms is 4 units then distance between two X atoms in *trans* position is .....
- Out of  $CH_2Cl_2$ ,  $CH_4$ ,  $CCl_4$ ,  $H_2O$ ,  $CHCl_3$ , *d*-dichlorobenzene, *o*-cresol, *p*-xylene,  $SCl_2$ ,  $BF_3$ ,  $LiCl$  and  $CH_2O$ , non-zero value of dipole moment is .....
- Superoxide ion has ..... electrons in anti-bonding molecular orbitals.
- Difference of  $\sigma$  and  $\pi$  bonds in  $C(CN)_4$  is .....



# Answers & Solutions

## Master Exercises

### Exercise 1

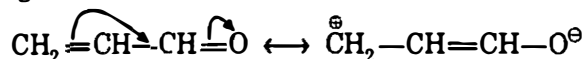
#### Short Answer Type Questions

1. The  $\text{NH}_3$  molecule has a dipole moment because the three N—H bond dipoles add to give a net dipole pointing upward to the N atom from the base of the pyramid that defines the  $\text{NH}_3$  structure.

The  $\text{SF}_6$  molecule has no dipole moment because each S—F bond dipole is balanced by one of equal magnitude pointing in opposite direction of the other side of the molecule.

2. (a) CH and CO bonds are polar.

(b) The CO bond is most polar, and O-atom is the most negative atom.



3. Bond-order NO is

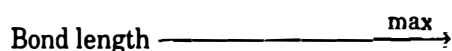
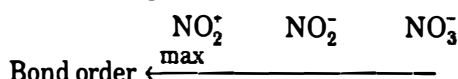
2 in  $\text{NO}^{2+}$

1.5 in  $\text{NO}_2^+$

1.33 in  $\text{NO}_3^-$

Thus, longest NO bond in  $\text{NO}_3^-$  and shortest in  $\text{NO}_2^+$

**Fact:** Larger the bond-order, shorter the bond-length



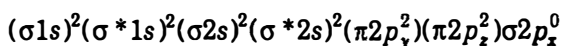
4. (a) The bond angle is smaller in  $\text{NH}_3$  than in  $\text{CH}_4$  because of the repulsion between the lone pair on N and the bonding pairs.
- (b) The bond angle is greater in  $\text{OCl}_2$  than in  $\text{OF}_2$  because there is some  $\pi$  interactions in  $\text{OCl}_2$  involving donation from the filled  $p$ -orbitals on oxygen into the empty  $d$ -orbitals on chlorine. No  $\pi$ -bonding is possible for  $\text{OF}_2$  because all orbitals are filled on both atoms.
- (c) The bond angle in  $\text{NH}_3$  is larger than that in  $\text{NF}_3$  because the N—F bonds are larger than N—H bonds and the electron density is displaced towards the more electronegative F, both effects diminish the bonding pair-bonding pair repulsion.
- (d) The bond angle in  $\text{NH}_3$  is larger than in  $\text{PH}_3$  because the P—H bonds are longer and the lower electronegativity of P permits electron-density to be displaced towards hydrogen to a greater extent than in the case of  $\text{NH}_3$ . Both of these effects diminish the repulsion due to bond-pairs.

5.  $\text{C} : 1s^2 2s^2 2p^2$ .

We consider formation of two  $sp$ -hybrid orbitals, one directed toward oxygen and directed  $180^\circ$  opposite. This contains carbon lone pair, leaving empty  $sp$  hybrid orbitals with a filled oxygen  $\sigma$ -orbital.

The two unhybridised singly occupied carbon  $2p$ -orbitals form  $\pi$  bonds by overlap with singly occupied oxygen  $2p$  orbitals.

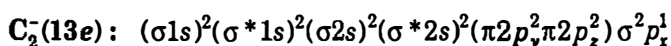
6.  $\text{C}_2$  (12  $e$ ) has molecular orbital electronic configuration as:



Bond-order

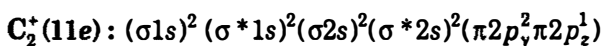
$$= \frac{\text{Electrons in (bonding MO - anti-bonding MO)}}{2}$$

$$= \frac{8 - 4}{2} = 2$$



$$\text{Bond-order} = \frac{9 - 4}{2} = 2.5$$

Electron is added to higher energy orbital ( $\sigma 2p_x$ ) and bond-order increases.

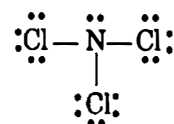


$$\text{Bond-order} = \frac{7 - 4}{2} = 1.5$$

Electron is removed from lower-energy orbital and bond-order decreases. This bond-dissociation energy of  $\text{C}_2^+$  is much lower than of  $\text{C}_2^-$  in which bond-order is higher and also electron is added to higher energy orbital.

#### Analytical Questions

1. (a) Two valence electrons missing, S and C have incomplete octet,  $[\text{:}\ddot{\text{S}}=\text{C}=\ddot{\text{N}}\text{:}]^-$ ,
- (b) Correct,
- (c) One valence electron missing; odd electron species with structure  $\ddot{\text{O}}=\ddot{\text{N}}=\ddot{\text{O}}\cdot$
- (d) N cannot have an expanded octet, correct structure is:



|    |            | $v$ | $s$ | $u$ | $F = v - \frac{s}{2} - u$ |
|----|------------|-----|-----|-----|---------------------------|
| 2. | (a) O      | 6   | 2   | 6   | -1                        |
|    | Cl         | 7   | 6   | 2   | +2                        |
|    | (b) S      | 6   | 8   | 2   | 0                         |
|    | O          | 6   | 4   | 4   | 0                         |
|    | (c) B      | 3   | 8   | 0   | -1                        |
|    | F          | 7   | 2   | 6   | 0                         |
|    | (d) N      | 5   | 8   | 0   | 1                         |
|    | (centre)   |     |     |     |                           |
|    | N          | 5   | 4   | 4   | -1                        |
|    | (terminal) |     |     |     |                           |
|    | (e) N      | 5   | 8   | 0   | +1                        |
|    | (centre)   |     |     |     |                           |
|    | N          | 5   | 2   | 6   | -2                        |
|    | (left)     |     |     |     |                           |
|    | N          | 5   | 6   | 2   | 0                         |
|    | (right)    |     |     |     |                           |
|    | (f) N      | 5   | 8   | 0   | +1                        |
|    | O          | 6   | 4   | 4   | 0                         |

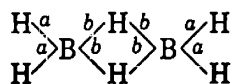
3. (b) Structure with the highest bond order and the shortest bond length ( $N \equiv N$ )

4. BE of fission of 6 (P—P) bond in  $P_4$  is greater than 6 (N—N) bond in  $N_4$ ; and BE of ( $N \equiv N$ ) is greater than that of ( $P \equiv P$ ).

5. The glowing of lamp tells us that the solid conducts when in molten state in which there are ions which are free to move. This also suggest that  $PbBr_2$  is ionic.

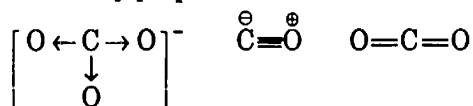
6. (a) Which are formed by two electrons.

(b) Which are formed by one electron.



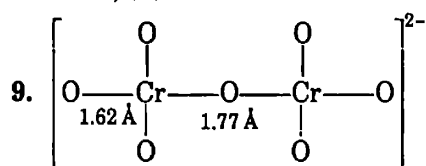
7. N and F both have high electron density due to smaller atomic radii. Thus,  $lp-bp$  repulsion increases bond-length.

8. Bond-length is inversely proportional to bond-order



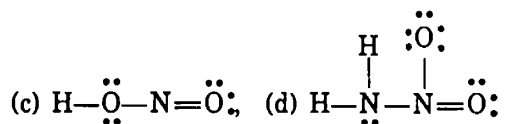
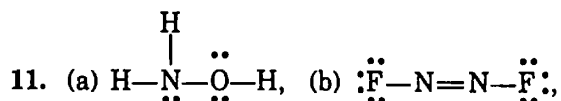
Bond-order : between 2 and 3      3      2

Thus, (d)

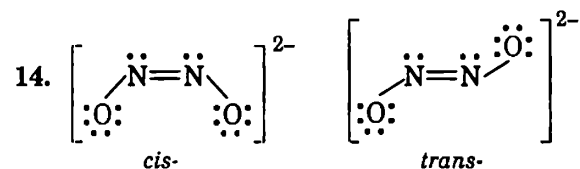
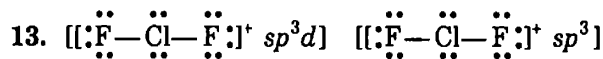


Thus, (b)

10.  $NI_3$  and  $SO_3^{2-}$  are trigonal pyramidal;  $I_3^-$  is linear and  $NO_3^-$  is trigonal planar.



12.  $PCl_5$  :  $sp^3d$  trigonal bipyramidal,  $BrF_5$   $sp^3d^2$  square based pyramid.



Since the  $\pi$ -bond between the nitrogen atoms must be broken to interconvert these two forms, hence, this ion will show *cis-trans* isomerisation.

| 15. | Atom | %    | Atomic mass | Mol  | Molar ratio |
|-----|------|------|-------------|------|-------------|
|     | Xe   | 60.4 | 131.3       | 0.46 | 1           |
|     | O    | 22.1 | 16.0        | 1.38 | 3           |
|     | F    | 17.5 | 19.0        | 0.92 | 2           |

Thus, empirical formula =  $XeO_3F_2$

Empirical formula weight = 217.3

Molar mass = 217.3

Molecular formula =  $XeO_3F_2$

16. I. (a) II. one  $\sigma$ , two  $\pi$

17.  $N_2$  : 1.10 Å linear,  $sp$  hybrid

$N_2F_2$  : 1.22 Å trigonal planar,  $sp^2$  hybrid

$N_2H_2$  : 1.45 Å tetrahedral,  $sp^3$  hybrid

18. (a) Cl (b) N (c) S (d) N

| 19. | Atom        | %     | Atomic mass/<br>Molar masses | Mol   | Molar ratio |
|-----|-------------|-------|------------------------------|-------|-------------|
|     | Co          | 21.24 | 58                           | 0.367 | 1           |
|     | $NH_3$      | 24.77 | 17                           | 1.46  | 4           |
|     | $SO_4^{2-}$ | 34.65 | 96                           | 0.36  | 1           |
|     | $H_2O$      | 6.53  | 18                           | 0.36  | 1           |
|     | Cl          | 12.81 | 35.5                         | 0.36  | 1           |

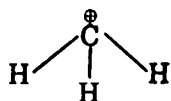
Empirical formula  $Co(NH_3)_4SO_4 \cdot H_2OCl$

The compound gives white ppt with  $BaCl_2$

Hence,  $SO_4$  is outside coordination sphere  
 $[Co(NH_3)_4(Cl)(H_2O)]SO_4$

20. In  $N(CH_3)_3$ , lone pair on N remains on it causing  $lp-bp$  repulsion while in  $N(SiH_3)_3$ , lone pair is transferred to vacant  $d$ -orbital of Si.

21. (a)
- $\overset{+}{\text{C}}\text{H}_3$
- has three orbitals



Thus, C-atom is  $sp^2$  hybrid with **triangular planar** structure

- (b) Silver acetylide is
- $\text{Ag}_2\text{C}_2$
- (
- $\text{AgC}\equiv\text{CAg}$
- )

Thus, C-atom is  $sp$ -hybridised.

- 22.
- $sp^3$
- , +2,
- 

23. (
- $\text{NF}_3$
- ,
- $\text{H}_3\text{O}^+$
- ) and (
- $\text{NO}_3^-$
- ,
- $\text{BF}_3$
- ) pairs isostructural.

- 24.
- $\text{KO}_2$
- has superoxide ion
- $\text{O}_2^-$
- with 17 electrons. Thus, one electron remains unpaired making it paramagnetic.

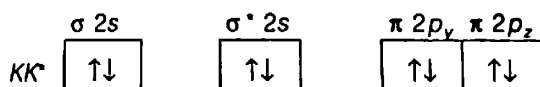
25. Trigonal planar,
- $sp^2$
26. Refer VSEPR theory.

27. Allene is
- $\text{CH}_2=\text{C}=\text{CH}_2$
28. (b) 29. (d)



30. Refer text 31. Refer text

32. (a) and (b) both have 12 electrons.



33. Total electrons = 2
- 
- $\sigma 1s^2$

bond order = 1, stable.

34. (a) Refer Table 2.10 :

| Species        | Bond order | Comparison of bond order    | Comparison of bond distance |
|----------------|------------|-----------------------------|-----------------------------|
| $\text{N}_2$   | 3          | $\text{N}_2 > \text{N}_2^+$ | $\text{N}_2 < \text{N}_2^+$ |
| $\text{N}_2^+$ | 2.5        |                             | increases                   |
| $\text{O}_2$   | 2          | $\text{O}_2^+ > \text{O}_2$ | $\text{O}_2^+ < \text{O}_2$ |
| $\text{O}_2^+$ | 2.5        |                             | decreases                   |

35. Calculated value of
- $\mu = e \times l$

$$= 4.8 \times 10^{-10} \text{ esu} \times 1.51 \times 10^{-10} \text{ cm}$$

$$= 7.248 \times 10^{-18} \text{ esu cm}$$

$$(1 \times 10^{-18} \text{ esu-cm} = 1 \text{ Debye}) = 7.248 \text{ Debye}$$

Observed value of  $\mu = 0.79 \text{ Debye}$

$$\% \text{ ionic character} = \frac{\text{observed value} \times 100}{\text{calculated value}}$$

$$= \frac{0.79}{7.248} \times 100$$

$$= 10.9\%$$

36. (a)
- $\text{:}\ddot{\text{F}}-\ddot{\text{N}}=\ddot{\text{O}}\text{:}$
- (b) angular (bent)

(c) larger  $\mu$  is a result of the molecule being asymmetric (bent) and having rather larger (EN) difference.  $\text{NO}_2\text{F}$  molecule has a symmetric shape.

- 37.
- $\mu_{cis} > \mu_{trans}$
- (= 0)

- 38.
- $l = \text{length} = 4 \times 10^{-11} \text{ m} = 4 \times 10^{-9} \text{ cm}$

$$e = \text{charge} = 4.8 \times 10^{-10} \text{ esu.}$$

$$\therefore \mu = e \times l = 4.8 \times 10^{-10} \times 4 \times 10^{-9} \text{ esu-cm}$$

$$= 1.92 \times 10^{-18} \text{ esu-cm} = 1.92 \text{ D}$$

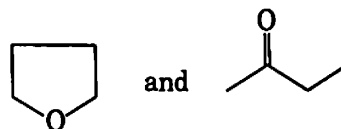
$$\text{Since, } 1 \text{ D} = 3.3 \times 10^{-30} \text{ C-m}$$

$$\mu = 1.92 \times 3.33 \times 10^{-30} \text{ C-m}$$

$$\therefore = 6.4 \times 10^{-30} \text{ C-m}$$

39. C—O single bond length =
- $0.77 + 0.66 = 1.43 \text{ \AA}$

C=O double bond length =  $1.22 \text{ \AA}$  (given). It is very near to predicted for a double bond. Hence, structure are :



40. (a)
- $sp^2$
- (b) II

- 41.
- $\mu = e \times l$

$$\mu = 2.9 \text{ D} = 2.9 \times 10^{-10} \text{ esu-cm}$$

$$e = 4.8 \times 10^{-10} \text{ esu.}$$

$$\therefore l = \frac{\mu}{e} = \frac{2.9 \times 10^{-18} \text{ esu-cm}}{4.8 \times 10^{-10} \text{ esu}}$$

$$= 6.04 \times 10^{-9} \text{ cm} = 0.0604 \text{ nm}$$

42. 0.0308 nm, No since
- $\mu \neq 0$

43. I.
- $D < A < B < C$
- II. (a)

- 44.
- $\text{LiF} > \text{LiF}_2$
- ,
- $\text{CsO} > \text{Cs}_2\text{O}$
- ,
- $\text{CaBr}_2 > \text{CaBr}_3$

- 45.
- $\text{C}-\text{H} < \text{Br}-\text{H} < \text{Na}-\text{I} < \text{F}-\text{H} < \text{Li}-\text{Cl} < \text{K}-\text{F}$

46. Refer text

47. Hydration energy of

$$\text{AlCl}_3 = \Delta H_{\text{Hyd}}(\text{Al}^{3+}) + 3\Delta H_{\text{Hyd}}(\text{Cl}^-)$$

$$= -4665 - 3 \times 381$$

$$= -5808 \text{ kJ mol}^{-1}$$

$$\text{IE of AlCl}_3 = 5137 \text{ kJ mol}^{-1}$$

Since, hydration energy  $>$  IE, hence,  $\text{AlCl}_3$  ionises (by hydration energy) thus it is ionic in aqueous solution.

48. I. (d)

II.  $\text{Ni}(\text{CO})_4$  and  $\text{Ni}(\text{CN})_4^{2-}$  are diamagnetic,  $\text{NiCl}_4^{2-}$  is paramagnetic.

III.  $sp^3-sp$  IV.  $\text{NCO}^-$ ,  $\text{CS}_2$ ,  $\text{NO}_2^+$  V.  $\text{S} < \text{Cl} < \text{N} < \text{O} < \text{F}$

49. I.
- $sp^3$
- II. absence of bond polarity III. four

IV.  $\text{CN}^-$ ,  $\text{NO}^+$  (each has 14 electrons)

50. (c) (I)
- 
- (II)
- $\text{H}_3\text{O}^+$
- ,
- $\text{NH}_3$
- ,
- $\text{CH}_3^-$

51. There is intramolecular H-bonding in
- o*
- hydroxybenzaldehyde (weak) while intermolecular H-bonding in
- p*
- isomer (strong).

52.  $\text{NO}_2$  has one unpaired electron, hence paramagnetic. On cooling, there is formation of new N—N bond (in  $\text{N}_2\text{O}_4$ ) using this unpaired electron; hence, paramagnetism is lost and molecular weight increases.



Resonance forms are only multiple representation of the same structure.

53. Refer sec. 7.15. Due to resonance in conjugate diene  
54. (c)

### NCERT Problems

Refer Text

## Exercise 2

### Only One Option Correct

- |          |          |          |          |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 1. (b)   | 2. (d)   | 3. (d)   | 4. (c)   | 5. (a)   | 6. (a)   | 7. (c)   | 8. (b)   | 9. (a)   | 10. (d)  |
| 11. (d)  | 12. (c)  | 13. (b)  | 14. (c)  | 15. (c)  | 16. (a)  | 17. (b)  | 18. (c)  | 19. (c)  | 20. (a)  |
| 21. (b)  | 22. (d)  | 23. (a)  | 24. (a)  | 25. (b)  | 26. (b)  | 27. (b)  | 28. (c)  | 29. (b)  | 30. (d)  |
| 31. (c)  | 32. (d)  | 33. (a)  | 34. (d)  | 35. (c)  | 36. (c)  | 37. (a)  | 38. (c)  | 39. (a)  | 40. (b)  |
| 41. (d)  | 42. (a)  | 43. (a)  | 44. (c)  | 45. (c)  | 46. (a)  | 47. (d)  | 48. (a)  | 49. (c)  | 50. (d)  |
| 51. (d)  | 52. (a)  | 53. (b)  | 54. (b)  | 55. (c)  | 56. (b)  | 57. (c)  | 58. (c)  | 59. (a)  | 60. (c)  |
| 61. (b)  | 62. (c)  | 63. (b)  | 64. (d)  | 65. (c)  | 66. (c)  | 67. (d)  | 68. (d)  | 69. (a)  | 70. (a)  |
| 71. (d)  | 72. (c)  | 73. (d)  | 74. (c)  | 75. (c)  | 76. (a)  | 77. (b)  | 78. (c)  | 79. (a)  | 80. (b)  |
| 81. (b)  | 82. (d)  | 83. (b)  | 84. (c)  | 85. (a)  | 86. (c)  | 87. (a)  | 88. (b)  | 89. (c)  | 90. (d)  |
| 91. (b)  | 92. (b)  | 93. (d)  | 94. (b)  | 95. (c)  | 96. (b)  | 97. (a)  | 98. (b)  | 99. (b)  | 100. (a) |
| 101. (c) | 102. (d) | 103. (d) | 104. (a) | 105. (d) | 106. (a) | 107. (a) | 108. (b) | 109. (d) | 110. (d) |
| 111. (a) | 112. (b) | 113. (b) | 114. (a) | 115. (a) | 116. (d) | 117. (b) | 118. (d) | 119. (a) | 120. (c) |
| 121. (c) | 122. (b) | 123. (a) | 124. (a) | 125. (b) | 126. (b) | 127. (c) | 128. (b) | 129. (a) | 130. (a) |
| 131. (c) | 132. (d) | 133. (d) | 134. (b) | 135. (d) | 136. (a) | 137. (a) | 138. (c) | 139. (a) | 140. (a) |

### One or More Than One Options Correct

1. (a, c)    2. (b, c)    3. (a, b)    4. (b, c, d)  
5. (a, b, d)    6. (b)    7. (c)    8. (d)    9. (a)  
10. (a)    11. (a, b, c)    12. (b)    13. (a, b, c)  
14. (a)    15. (a), (b)    16. (a)    17. (a, c, d)  
18. (a, b, c, d)    19. (c)    20. (b, c)

### Passage Comprehension Questions

#### Passage 1

1. (c)    2. (c)    3. (a)

#### Passage 2

1. (b)    2. (d)    3. (a)

#### Passage 3

1. (a)    2. (a)    3. (b)

#### Passage 4

1. (a)    2. (d)    3. (c)

#### Passage 5

1. (b)    2. (d)    3. (b)    4. (a)

#### Passage 6

1. (c)    2. (a)    3. (d)    4. (b)

#### Passage 7

1. (a)    2. (b)

#### Passage 8

1. (d)    2. (c)

#### Passage 9

1. (a)    2. (c)    3. (b)    4. (a), (b)    5. (a), (c)

#### Passage 10

1. (c)

#### Passage 11

1. (c)    2. (d)    3. (b)

### Assertion & Reason

1. (a)    2. (a)    3. (b)    4. (a)    5. (b)    6. (c)  
7. (d)    8. (a)    9. (c)    10. (a)    11. (a)    12. (b)  
13. (a)

## True & False

1. T    2. F    3. F    4. F    5. T    6. F    7. T  
8. T    9. F    10. T    11. T    12. F    13. F    14. F  
15. T    16. F    17. F    18. T    19. T    20. T

## Fill in the Blanks

1. square planar
2. Fajan's rule
3.  $4^\circ$
4. paramagnetic
5. H-bonding
6. ionic
7. sigma
8. Lewis base, Lewis acid
9. ionic (between  $\text{NH}_4^+$  and  $\text{Cl}^-$ ), covalent (between N and H), coordinate (between  $\text{H}^+$  and  $\text{NH}_3$ ).
10. paramagnetic, diamagnetic
11. 2, 1.5, 1 oxygen, superoxide ion
12.  $sp^2, sp^2, sp^3$
13.  $dsp^2, sp^3$
14.  $\sqrt{24}$  BM
15. 1.7
16.  $\text{NH}_3, \text{PH}_3$
17. 4
18. increases, decreases
19. increases, decreases
20. large  $\text{N}\equiv\text{N}$  bond energy
21.  $\text{PCl}_4^+, \text{PCl}_6^-$
22. Lewis acid, Lewis base
23. electron sea model, band model
24. very large, very short
25. valence band, conduction band

### Matrix-Match Type Questions

### I. Only One Correct

1. (A)—(3); (B)—(1); (C)—(4); (D)—(2)  
 2. (A)—(3); (B)—(2); (C)—(1)  
 3. (A)—(3); (B)—(1); (C)—(4); (D)—(2)  
 4. (A)—(4); (B)—(3); (C)—(1); (D)—(2)  
 5. (A)—(6); (B)—(2); (C)—(3); (D)—(1)  
 6. (A)—(2); (B)—(3); (C)—(1); (D)—(4);  
 (E)—(6)  
 7. (A)—(3); (B)—(5); (C)—(6); (D)—(1);  
 (E)—(4);  
 8. (A)—(4); (B)—(2); (C)—(1); (D)—(3)  
 9. (A)—(3); (B)—(1); (C)—(2); (D)—(4)  
 10. (A)—(3); (B)—(4); (C)—(2); (D)—(1)

| 11. | List I            | List II | List III |
|-----|-------------------|---------|----------|
|     | $\text{Be}_2^+$   | 0.5     | 1        |
|     | $\text{O}_2$      | 2.0     | 2        |
|     | $\text{O}_2^+$    | 2.5     | 1        |
|     | $\text{O}_2^{2-}$ | 1.0     | 0        |

- 12.**

| List I          | List II | List III                    |
|-----------------|---------|-----------------------------|
| NO <sup>+</sup> | 3.0     | N <sub>2</sub>              |
| NO              | 2.5     | O <sub>2</sub> <sup>+</sup> |
| NO <sup>-</sup> | 2.0     | O <sub>2</sub>              |

## II. One or More Correct

1. (A)—(3,4); (B)—(5,6); (C)—(1); (D)—(2,3);  
(E)—(1)
2. (A)—(1,5); (B)—(1,3); (C)—(3); (D)—(2,4);  
(E)—(3,5)

## Integer Answer Types

## Set I

|             |   |   |   |   |   |   |   |   |
|-------------|---|---|---|---|---|---|---|---|
| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Answers →   | 4 | 4 | 3 | 3 | 6 | 1 | 0 | 3 |
|             | ① | ① | ① | ① | ① | ① | ① | ① |
|             | ① | ① | ① | ① | ① | ① | ① | ① |
|             | ② | ② | ② | ② | ② | ② | ② | ② |
|             | ③ | ③ | ③ | ③ | ③ | ③ | ③ | ③ |
|             | ④ | ④ | ④ | ④ | ④ | ④ | ④ | ④ |
|             | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ |
|             | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ |
|             | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ |
|             | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ |
|             | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ |

## Set II

[illegible]

The members of the same group of elements (arranged as every eighth in a group) stand to each other in the same relation as the extremities of one or more octaves in music.

John Newlands



# Periodicity of Elements

## Quick Points

Electrons in various subshells of a shell (orbit) are filled based on

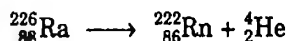
—Aufbau rule

—Hund's rule

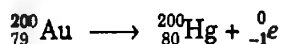
—Pauli's exclusion rule

- $\alpha$ -particle is positively charged helium nucleus

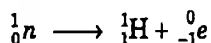
Its emission causes decrease in atomic number by two units and atomic mass by four units



Emission of  $\beta$ -particle increases atomic number by one unit resulting in the formation of isobar.



This is due to conversion of neutron to proton



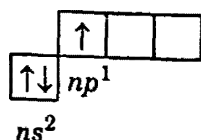
- $ns^2$  pair in  $p$ -block elements is inert if it can't be unpaired (inert-pair effect). If a  $p$ -block element  $M^{x+}$  does not have noble gas configuration ( $n^2np^6$  or  $1s^2$  (He)) then it is expected to show inert-pair effect where  $x$  is the number of valence electrons.

| Atom | Z  | E.C.                       | x | $M^{x+}$  | E.C.             | Inert pair effect |
|------|----|----------------------------|---|-----------|------------------|-------------------|
| B    | 5  | $1s^2 2s^2 2p^1$           | 3 | $B^{3+}$  | $1s^2$           | No                |
| Al   | 13 | $1s^2 2s^2 2p^6 3s^2 3p^1$ | 3 | $Al^{3+}$ | $1s^2 2s^2 2p^6$ | No                |
| Ga   | 31 | $[Ar] 3d^{10} 4s^2 4p^1$   | 3 | $Ga^{3+}$ | $[Ar] 3d^{10}$   | Yes               |
| P    | 15 | $1s^2 2s^2 2p^6 3s^2 3p^3$ | 5 | $P^{5+}$  | $1s^2 2s^2 2p^6$ | No                |
| As   | 33 | $[Ar] 3d^{10} 4s^2 4p^3$   | 5 | $As^{5+}$ | $[Ar] 3d^{10}$   | Yes               |

## Learning Framework of the Chapter

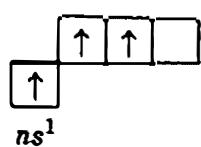
- The Origin of The Periodic Table
- Classification of the Elements in Blocks
- Periodicity
- Valency and Oxidation Number
- Shielding (Screening) Effect and Effective Nuclear Charge
- Size of an Atom and Ion
- Ionisation Energy
- Electron Affinity
- Electronegativity
- Metallic Nature
- Hydration and Hydration Energy
- Acid-Base Character of Oxides
- Hydrides
- Melting Points and Boiling Points
- Density
- Atomic Volume

Ga [Ar]  $3d^{10}$   
(ground state)



valency +1 if  $ns^2$   
pair is inert.

Ga (first excited state)  
[Ar]  $3d^{10}$



valency +3 if  $ns^2$   
pair is excited, and  
thus three unpaired  
electrons take part  
in chemical bonding.

(For detail refer Inert-Pair Effect in Chemical-Bonding Chapter-2)

The concept of chemical periodicity is central to the study of Inorganic Chemistry. Chemical periodicity and the Periodic Table now find their natural interpretation in the detailed electronic structure of atom; indeed they played a major role at the turn of the century in elucidating the mysterious phenomenon of radioactivity and the quantum effects which led ultimately to Bohr's theory of the H-atom.

## The Origin of The Periodic Table

- A brief historical survey of various development in the study of Periodic Table is given in Table 3.1. There is no single best form of the Periodic Table since the choice depends on the purpose for which the table is used. The most convenient form for various studies is "long form" with separate panels for the actinide and lanthanide elements.
- There has always been confusion over the numbering system to be used for the individual groups in the table. We adopt the 1-18 numbering scheme recommended by IUPAC in 1988. The 'long form' of the Periodic Table is given in Table 3.2. For comparison, numbering in Roman digits I, II, .... is also given.
- One advantage of the IUPAC system is that the groups headed by Fe, Co, and Ni have separate designations (8, 9 and 10, respectively) instead of all being placed together in VIII B. Also, for the transition elements

group number = number of electrons in  $(n-1)d$  and  $ns$  orbitals

and for the  $p$ -block elements

group number = 10 + outer-shell electrons

**Table 3.1 Mendeleef's Periodic Table**

### Precursors and Successors

**1772** L.B.G. de Morveau made the first table of "chemically simple" substances. A. L. Lavoisier used this in his *traité Élémentaire de Chimie* published in 1789.

**de Morveau's Table of Chemically Simple Substances**

de Morveau's table of chemically simple substances (updated with modern representations by Mazurs):

| Non Decomposable Substances |                               |                     |    |                                |                    |
|-----------------------------|-------------------------------|---------------------|----|--------------------------------|--------------------|
| Simple substances           | Simple combustible substances | Metallic substances |    | Simple earths                  | Alkalies           |
|                             | N                             | As                  | Fe | SiO <sub>2</sub>               | NaOH               |
|                             | C                             | Mo                  | Sn | Al <sub>2</sub> O <sub>3</sub> | KOH                |
| O                           | S                             | W                   | Pb | BaO                            | NH <sub>4</sub> OH |
| H                           | P                             | Mn                  | Cu | CaO                            |                    |
|                             | Cl                            | Ni                  | Hg | MgO                            |                    |
|                             | B                             | Co                  | Ag |                                |                    |
|                             | F                             | Bi                  | Pt |                                |                    |
|                             | etc.                          | Sb                  | Au |                                |                    |
|                             |                               | Zn                  |    |                                |                    |

**1817-29** J.W. Döbereiner discovered many triads of elements and compounds, the combining weight of the central component being the average of its partners (e.g. CaO, SrO, BaO, and NiO, CuO, ZnO).

**1850** Johann Dobereiner's Triads (1780-1849)

Triads are found with sequence of three similar elements, where the middle element has a mass equal to the average of the least and most massive. The diagram below, updated from here, uses mid-nineteenth century atomic mass information rather than modern data. If atomic number ( $Z$ ) are used (a property unknown in 1850), the triads are exact:

| Atomic mass (1850) |                                         |  | Atomic number |                                      |  |
|--------------------|-----------------------------------------|--|---------------|--------------------------------------|--|
| Li 7]              |                                         |  | Li 3]         |                                      |  |
| Na 23]             | $\rightarrow \frac{7 + 39}{2} = 23$     |  | Na 11]        | $\rightarrow \frac{3 + 19}{2} = 11$  |  |
| K 39]              |                                         |  | K 19]         |                                      |  |
| Ca 40]             |                                         |  | Ca 20]        |                                      |  |
| Sr 87]             | $\rightarrow \frac{40 + 137}{2} = 88.5$ |  | Sr 38]        | $\rightarrow \frac{20 + 56}{2} = 38$ |  |
| Ba 137]            |                                         |  | Ba 56]        |                                      |  |
| P 31]              |                                         |  | P 15]         |                                      |  |
| As 75]             | $\rightarrow \frac{31 + 122}{2} = 76.5$ |  | As 33]        | $\rightarrow \frac{15 + 51}{2} = 33$ |  |
| Sb 122]            |                                         |  | Sb 51]        |                                      |  |
| S 32]              |                                         |  | S 16]         |                                      |  |
| Se 78]             | $\rightarrow \frac{32 + 128}{2} = 80$   |  | Se 34]        | $\rightarrow \frac{16 + 52}{2} = 34$ |  |
| Te 128]            |                                         |  | Te 52]        |                                      |  |
| Cl 35.5]           |                                         |  | Cl 17]        |                                      |  |
| Br 80]             | $\rightarrow \frac{35.5 + 127}{2}$      |  | Br 35]        | $\rightarrow \frac{17 + 53}{2} = 35$ |  |
| I 127]             |                                         |  | I 53]         |                                      |  |
| = 81.25            |                                         |  |               |                                      |  |

|    |    |    |    |    |    |    |    |  |  |  |    |
|----|----|----|----|----|----|----|----|--|--|--|----|
| H  |    |    |    |    |    |    |    |  |  |  | He |
| Li | Be | B  | C  | N  | O  | F  | Ne |  |  |  |    |
| Na | Mg | Al | Si | P  | S  | Cl | Ar |  |  |  |    |
| K  | Ca | Ga | Ge | As | Se | Br | Kr |  |  |  |    |
| Rb | Sr | In | Sn | Sb | Te | I  | Xe |  |  |  |    |
| Cs | Ba | Tl | Pb | Bi | Po | At | Rn |  |  |  |    |





## Main Features of Mendeleef's Periodic Classification

### Study and explanation of the table

In the table, the elements are arranged in order of their increasing atomic weights in horizontal series, in such a way that elements having similar properties are

placed in the same vertical column. The horizontal series are generally written as periods, and the nine vertical columns-headed by the Roman numerals from I to VIII and zero (0) are called groups. The periods are short or long.

### Periodic Table

Table 3.1 With Atomic numbers written above and Atomic weights written by the side of the Symbols

| Periods | Group I                                                                                    | Group II                                                                                       | Group III                                                                                      | Group IV                                                                                       | Group V                                                                                        | Group VI                                                                                       | Group VII                                                                                    | Group VIII                                                                                          | Group 0          |               |
|---------|--------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------|------------------|---------------|
|         | $R_2O$<br>$RH$<br>$\underbrace{\hspace{1cm}}_A \hspace{0.2cm} \underbrace{\hspace{1cm}}_B$ | $R_2O_2$<br>$RH_2$<br>$\underbrace{\hspace{1cm}}_A \hspace{0.2cm} \underbrace{\hspace{1cm}}_B$ | $R_2O_3$<br>$RH_3$<br>$\underbrace{\hspace{1cm}}_A \hspace{0.2cm} \underbrace{\hspace{1cm}}_B$ | $R_2O_4$<br>$RH_4$<br>$\underbrace{\hspace{1cm}}_A \hspace{0.2cm} \underbrace{\hspace{1cm}}_B$ | $R_2O_5$<br>$RH_3$<br>$\underbrace{\hspace{1cm}}_A \hspace{0.2cm} \underbrace{\hspace{1cm}}_B$ | $R_2O_6$<br>$RH_2$<br>$\underbrace{\hspace{1cm}}_A \hspace{0.2cm} \underbrace{\hspace{1cm}}_B$ | $R_2O_7$<br>$RH$<br>$\underbrace{\hspace{1cm}}_A \hspace{0.2cm} \underbrace{\hspace{1cm}}_B$ | $R_2O_8 \leftarrow$ formula of<br>oxides $\leftarrow$ formula of<br>hydrides.<br>$\hspace{1.5cm} A$ | or<br>Gr. VIII B |               |
| 1       |                                                                                            |                                                                                                |                                                                                                |                                                                                                |                                                                                                |                                                                                                | 1<br>H 1.008                                                                                 |                                                                                                     | 2<br>He 4        |               |
| 2       | 3<br>Li 6.94                                                                               | 4<br>Be 9.02                                                                                   | 5<br>B 10.82                                                                                   | 6<br>C 12                                                                                      | 7<br>N 14.01                                                                                   | 8<br>O 16                                                                                      | 9<br>F 19                                                                                    |                                                                                                     | 10<br>Ne 20.2    |               |
| 3       | 11<br>Na 23                                                                                | 12<br>Mg 24.3                                                                                  | 13<br>Al 26.97                                                                                 | 14<br>Si 28.06                                                                                 | 15<br>P 31.04                                                                                  | 16<br>S 32                                                                                     | 17<br>Cl 35.46                                                                               |                                                                                                     | 18<br>Ar 39.94   |               |
| 4       | 19<br>K 39.1                                                                               | 20<br>Ca 40                                                                                    | 21<br>Sc 45.1                                                                                  | 22<br>Ti 48.1                                                                                  | 23<br>V 51                                                                                     | 24<br>Cr 52                                                                                    | 25<br>Mn 54.9                                                                                | 26<br>Fe 55.8                                                                                       | 27<br>Co 58.9    | 28<br>Ni 58.6 |
|         | 29<br>Cu 63.5                                                                              | 30<br>Zn 65.3                                                                                  | 31<br>Ga 70                                                                                    | 32<br>Ge 72.5                                                                                  | 33<br>As 74.9                                                                                  | 34<br>Sc 79.2                                                                                  | 35<br>Br 79.9                                                                                |                                                                                                     |                  | 36<br>Kr 83.7 |
| 5       | 37<br>Rb 85.4                                                                              | 38<br>Sr 87.63                                                                                 | 39<br>Y 88.9                                                                                   | 40<br>Zr 91.2                                                                                  | 41<br>Nb 92.9                                                                                  | 42<br>Mo 96                                                                                    | 43<br>Tc 97.8                                                                                | 44<br>Ru 101.7                                                                                      | 45<br>Rh 103     | 46<br>Pd 106  |
|         | 47<br>Ag 107.8                                                                             | 48<br>Cd 112                                                                                   | 49<br>In 114.8                                                                                 | 50<br>Sn 119                                                                                   | 51<br>Sb 121.76                                                                                | 52<br>Te 127.6                                                                                 | 53<br>I 126.9                                                                                |                                                                                                     |                  | 54<br>Xe 131  |
| 6       | 55<br>Cs 132.9                                                                             | 56<br>Ba 137.37                                                                                | 57<br>La 139                                                                                   | 72<br>Hf 178.6                                                                                 | 73<br>Ta 180.8                                                                                 | 74<br>W 184                                                                                    | 75<br>Re 186.3                                                                               | 76<br>Os 191                                                                                        | 77<br>Ir 198     | 78<br>Pt 195  |
|         | 79<br>Au 197.2                                                                             | 80<br>Hg 200.6                                                                                 | 58-71<br>Rare Earths                                                                           | 82<br>Pb 207.2                                                                                 | 83<br>Bi 209                                                                                   | 84<br>Po 210                                                                                   | 85<br>—                                                                                      |                                                                                                     |                  | 86<br>Rn 222  |
|         |                                                                                            |                                                                                                | 81<br>Ti 204                                                                                   |                                                                                                |                                                                                                |                                                                                                |                                                                                              |                                                                                                     |                  |               |
| 7       | 87<br>—                                                                                    | 88<br>Ra 226                                                                                   | 89<br>Ac 227                                                                                   | 90<br>Th 232 12                                                                                | 91<br>Pa 231                                                                                   | 92<br>U 238.14                                                                                 |                                                                                              |                                                                                                     |                  |               |

### Short and Long Periods

| Period | Elements                                                                                                                                                            |
|--------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1      | H He (Short period)                                                                                                                                                 |
| 2      | Li Be B C N O F Ne<br>Electropositive Electronegative Inert                                                                                                         |
|        | There is a regular change from the strongly electropositive element Li to the strongly electronegative element F, which is followed by the inert element Ne.        |
| 3      | Na Mg Al Si P S Cl A                                                                                                                                                |
|        | There is same periodicity as in second period. Na resembles Li; Mg resembles Be; Al resembles B and so on. Such periods of eight elements are called short periods. |

- The fourth period begins with K which strongly resembles Na; but in this case we have to pass over 18 elements (instead of 8) before another element Rb (rubidium) strongly resembling K is reached. Such a period of 18 elements is called **Long period**. K<sub>19</sub> ——— Kr (36)
- Rb ——— Xe of 18 elements is another long period. The abrupt increase from 8 to 18 elements in passing from the short to the long period is due to the interpolation of so called transitional elements.
- Cs ——— Rn consists of 32 elements and is therefore called a very long period, or a monster period. This increase from 18 to 32 elements is due to the introduction of 14 rare-earth elements.
- It is fragmentary. It starts like a long period, but soon comes to an end. Uranium (at fifth place) is the element of highest atomic weight known at that time.

## Intervals of Periodicity

Thus, we observe that intervals of periodicity are  $2n^2$  ( $n$  = period), i.e., 2, 8, 18, 18, 32

**Even series** The first seven elements of a long period form the even series.

**Odd series** The last seven elements of a long period form the odd series.

**Group Zero** The inert gases like helium, argon, etc. present in the air were discovered afterwards. They were placed in zero group. They being inert and having no valency, stands between the highly electropositive alkali metals and the strongly electronegative halogens.

|                      |                |                      |
|----------------------|----------------|----------------------|
| F<br>Cl<br>Br        | Ne<br>Ar<br>Kr | Na<br>K<br>Rb        |
| ↑                    | ↑              | ↑                    |
| Most electronegative | Inert          | Most electropositive |

Partington considered group zero as sub group B of group VIII.

**Subgroups** Each group is divided into subgroup A and B. The elements belonging to the even series of their respective long periods are placed to the left (sub group A), while those belonging to the odd series are arranged on the right-hand side (subgroup B) of each vertical column. The members belonging to a subgroup are more closely related than the other members of the same group.

**The Rare Earths** Lanthanum in Group III and in the 6th period forms a cluster with 14 other elements (atomic number 58-71) which have got atomic weights differing by one or two or four; they are analogous in chemical properties, and it is very difficult to separate them in analysis. They are known as the **elements of the rare earths**.

**The Radioactive Elements** There is also a class of elements, placed in last period of the Periodic Table, which differ from the rest in as much as they are *radioactive*, i.e., they constantly liberate energy, which appears to be derived from the disintegration of atoms.

Periodicity in the properties of the elements, when arranged in the Periodic Table is shown in terms of.

**1. Valency** The valencies towards hydrogen regularly increase up to the middle of a short period and then gradually fall and come back to unity. The valencies towards oxygen, on the other hand increase regularly from 1 to 7, and then begin with 1. Elements of group zero have zero valency.

|                   |                  |                                |                  |                               |                 |                                |
|-------------------|------------------|--------------------------------|------------------|-------------------------------|-----------------|--------------------------------|
| LiH               | BeH <sub>2</sub> | BH <sub>3</sub>                | CH <sub>4</sub>  | NH <sub>3</sub>               | OH <sub>2</sub> | FH                             |
| 1                 | 2                | 3                              | 4                | 3                             | 2               | 1                              |
| Na <sub>2</sub> O | MgO              | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | N <sub>2</sub> O <sub>5</sub> | SO <sub>3</sub> | Cl <sub>2</sub> O <sub>7</sub> |
| 1                 | 2                | 3                              | 4                | 5                             | 6               | 7                              |

**2. Electrochemical Character** In group I, elements are highly electropositive. In between there are

non-metals (less electropositive) followed by electronegative elements as halogens

|    |    |    |    |   |   |    |
|----|----|----|----|---|---|----|
| Li | Be | B  | C  | N | O | F  |
| Na | Mg | Al | Si | P | S | Cl |

**3. Other Properties** The same periodicity in the properties can be observed with regard to the

- melting point
- boiling point
- specific gravity
- atomic volume

In atomic heat periodicity is not observed.

## Applications of the Periodic Law

### 1. In classification of the elements

(a) We can form an idea of the properties of an element and its compounds by knowing the group it belongs to

(b) We can compare the properties of different elements and their compounds belonging to different groups.

**2. In the prediction of new elements** When Mendeleef first prepared the Periodic Table, many blank spaces were automatically left in it. Space of the elements (not known at that time) Sc, Ga, Ge were left blank. However he predicted their properties by naming

eka-boron (below boron)  
eka-aluminium (below aluminium)  
eka-silicon (below silicon)

|                     |        |        |        |
|---------------------|--------|--------|--------|
|                     | B      | Al     | Si     |
| Named by Mendeleef] | Eka-B, | Eka-Al | Eka-Si |
| Named afterwards]   |        | Ga     | Ge     |

The following table summarises the predicted (15 years before discovery by Mendeleef in 1871) and observed (discovered by Winkler in 1886)

| Property                     | Ekosilicon (1871) | Germanium (discovered in 1886 by Winkler)        |
|------------------------------|-------------------|--------------------------------------------------|
| At. wt.                      | 72                | 72.3                                             |
| Sp. wt.                      | 5.5               | 5.469                                            |
| At. vol.                     | 13                | 13.2                                             |
| Oxide                        | EsO <sub>2</sub>  | GeO <sub>2</sub>                                 |
| Sp. wt. oxide                | 4.7               | 4.703                                            |
| Chloride                     | EsCl <sub>4</sub> | GeCl <sub>4</sub>                                |
| Boiling point chloride       | < 100°            | 86°                                              |
| Density chloride             | 1.9               | 1.887                                            |
| Fluoride                     | EsF <sub>4</sub>  | GeF <sub>4</sub> · 3H <sub>2</sub> O             |
| Not gaseous                  |                   | white solid mass                                 |
| Ethyl compound               | EsEt <sub>4</sub> | Ge(C <sub>2</sub> H <sub>5</sub> O) <sub>4</sub> |
| Boiling point ethyl compound | 160°              | 160°                                             |
| Sp. wt. ethyl compound       | 0.96              | a little < 1                                     |

\*Eka a prefix being the sanskrit numeral one

**3. In correcting doubtful atomic weight** An element has got only one proper place in the Periodic Table. Position is fixing by comparing its properties with those of neighbouring elements.

## Elements 113 and 115 Discovered

Two super heavy elements, element 113 and element 115, have been discovered by scientists. The team observed atomic decay patterns or chains, that confirm the existence of these two elements.

In these decay chains, element 113 is produced *via* the alpha decay of element 115. The observations were made in experiments conducted at the JINR (Joint Institute for Nuclear Research in Russia) U400 cyclotron with the Dubna gas-filled separator between July 14 and August 10, 2003. Scientists from the Glenn T. Seaborg Institute and the Chemical Biology and Nuclear Science Division at Lawrence Livermore National Lab, worked in collaboration with researchers from the JINR. The results have been published in *Physical Review C*.

## Modern Periodic Law

The properties of elements are periodic functions of their atomic numbers. If element are arranged in increasing order of their atomic numbers, there is repetition of properties after 2, 8, 8, 18, 18 and 32 elements. The numbers 2, 8, 18 and 32 are also referred as **magic numbers**.

Repetition of properties after these numbers is due to repetition of electronic configurations of the outermost orbit.

|                  |                                                                                                       |                                                                                                                                   |
|------------------|-------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------|
| H <sub>1</sub>   | 1s <sup>1</sup>                                                                                       | H to Fr have been placed together [in group 1 (IA)] due to the fact that outermost orbit has <b>ns<sup>1</sup></b> configuration. |
| Li <sub>3</sub>  | 1s <sup>2</sup> , 2s <sup>1</sup>                                                                     |                                                                                                                                   |
| Na <sub>11</sub> | 1s <sup>2</sup> , 2s <sup>2</sup> 2p <sup>6</sup> , 3s <sup>1</sup>                                   |                                                                                                                                   |
| K <sub>19</sub>  | 1s <sup>2</sup> , 2s <sup>2</sup> 2p <sup>6</sup> , 3s <sup>2</sup> 3p <sup>6</sup> , 4s <sup>1</sup> |                                                                                                                                   |
| Rb <sub>37</sub> | [Kr] 5s <sup>1</sup>                                                                                  |                                                                                                                                   |
| Cs <sub>55</sub> | [Xe] 6s <sup>1</sup>                                                                                  |                                                                                                                                   |
| Fr <sub>87</sub> | [Rn] 7s <sup>1</sup>                                                                                  |                                                                                                                                   |

## Long form (Modern form) of Periodic Table

It is annexed in Table 3.2. The elements have been arranged in the increasing order of **atomic number**.

- It can explain why certain elements resemble one another and also why they differ from other elements

in their properties. The arrangement of elements in this table is also in keeping with their electronic structures.

- This table also explains the cause of periodicity of properties (discussed in following sections) and the reason why similar properties recur at certain regular intervals.
- The horizontal rows constitute **periods** while the vertical rows constitute **groups** or **families**.
- 4th, 5th, 6th and 7th periods also include **transition** elements.
- 6th and 7th periods also include **inner transition** elements (rare-earth) and grouped at the bottom of the main Periodic Table.
- Elements (58-71) are called **lanthanides** while elements (90-103) are called **actinides**. Each is a group of 14 elements and grouped in IIIB. (3rd period)

## Explanation for Aufbau Principle

The arrangement of the long Periodic Table may be explained from the distribution of electrons in various quantum levels. Each period starts with an element having one valence electron in the s-orbital as given below :

| Element | Valence electron |
|---------|------------------|
| H       | 1s <sup>1</sup>  |
| Li      | 2s <sup>1</sup>  |
| Na      | 3s <sup>1</sup>  |
| K       | 4s <sup>1</sup>  |
| Rb      | 5s <sup>1</sup>  |
| Cs      | 6s <sup>1</sup>  |
| Fr      | 7s <sup>1</sup>  |

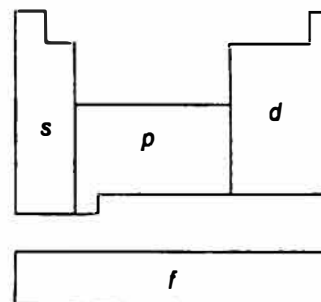
Electrons in various subshells have been filled based on Aufbau principle i.e.,

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 6d < 6p < 7s < 5f \dots$$

Thus, 3d orbital which is filled after 4s is a part of fourth period. Thus one can determine number of elements in a given period assuming two elements in s, six in -p, ten in -d and fourteen in f-suborbitals.

| Period | Suborbit | Elements | Total elements | Comment                     |
|--------|----------|----------|----------------|-----------------------------|
| 1      | 1s       | 2        | 2              |                             |
| 2      | 2s       | 2        | 8              |                             |
|        | 2p       | 6        |                |                             |
| 3      | 3s       | 2        | 8              |                             |
|        | 3p       | 6        |                |                             |
| 4      | 4s       | 2        | 18             | 3d is in 4th period         |
|        | 3d       | 10       |                |                             |
|        | 4p       | 6        |                |                             |
| 5      | 5s       | 2        | 18             | 4d is in 5th period         |
|        | 4d       | 10       |                |                             |
|        | 5p       | 6        |                |                             |
| 6      | 6s       | 2        | 32             | 4f and 5d are in 6th period |
|        | 4f       | 14       |                |                             |
|        | 5d       | 10       |                |                             |
|        | 6p       | 6        |                |                             |

The sixth period is further complicated by the filling of  $4f$ -orbitals after  $4d$ -orbitals. As  $4d$ -suborbit may accommodate maximum of 14 electrons, we have the first series of 14 inner-transition elements, each related to the entry of one electron in the  $4f$ -orbital. If these are placed in the Periodic Table, it would require 14 extra group; this would make the table unnecessarily long. Hence, these elements have been placed separately at the bottom of the Periodic Table. Similarly elements with  $5f$ -orbitals form a separate block.



- The eight families belonging to the  $s$ - and  $p$ -blocks are often called the representative elements; those to the  $d$ -block are called the transition elements and members of the  $f$ -block are termed the inner-transition elements.

| PERIODIC TABLE |        |        |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
|----------------|--------|--------|------------------------------------|-----|---------|-----|----|-----|-----|------|----|----|----|-----|---------|-----|----|-----|------|---------|
| PERIODS        |        |        |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
| SHORT          | 1 to 7 | GROUPS |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
|                |        |        | 1                                  | 2   | 3       | 4   | 5  | 6   | 7   | 8    | 9  | 10 | 11 | 12  | 13      | 14  | 15 | 16  | 17   | 18      |
| LONG           |        |        | IA                                 | IIA | IIIB    | IVB | VB | VIB | VII | VIII | IX | X  | IB | IIB | IIIA    | IVA | VA | VIA | VIIA | VIII(0) |
|                |        |        | s-block                            |     | d-block |     |    |     |     |      |    |    |    |     | p-block |     |    |     |      |         |
|                |        |        | f (in IIIB of 6th and 7th periods) |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
|                |        |        |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
|                |        |        |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
|                |        |        |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
|                |        |        |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
|                |        |        |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
|                |        |        |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
|                |        |        |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
|                |        |        |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
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|                |        |        |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
|                |        |        |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
|                |        |        |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
|                |        |        |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
|                |        |        |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |
|                |        |        |                                    |     |         |     |    |     |     |      |    |    |    |     |         |     |    |     |      |         |

| Group  | IA  | IIA | IIIB | IVB | VB  | VIB | VIIB | VIII |     |      | IB   | IIB  | IIIA | IVA  | VA   | VIA  | VIIA | 0    |
|--------|-----|-----|------|-----|-----|-----|------|------|-----|------|------|------|------|------|------|------|------|------|
|        | (1) | (2) | (3)  | (4) | (5) | (6) | (7)  | (8)  | (9) | (10) | (11) | (12) | (13) | (14) | (15) | (16) | (17) | (18) |
| Period | 1   |     |      |     |     |     |      |      |     |      |      |      |      |      |      |      | 1    | 2    |
| 1      | H   |     |      |     |     |     |      |      |     |      |      |      |      |      |      |      | H    | He   |
|        | 1s  |     |      |     |     |     |      |      |     |      |      |      |      |      |      |      | 1s   |      |
| 2      | 3   | 4   |      |     |     |     |      |      |     |      |      |      | 5    | 6    | 7    | 8    | 9    | 10   |
|        | Li  | Be  |      |     |     |     |      |      |     |      |      |      | B    | C    | N    | O    | F    | Ne   |
|        | 2s  |     |      |     |     |     |      |      |     |      |      |      | 2p   |      |      |      |      |      |
| 3      | 11  | 12  |      |     |     |     |      |      |     |      |      |      | 13   | 14   | 15   | 16   | 17   | 18   |
|        | Na  | Mg  |      |     |     |     |      |      |     |      |      |      | Al   | Si   | P    | S    | Cl   | Ar   |
|        | 3s  |     |      |     |     |     |      |      |     |      |      |      | 3p   |      |      |      |      |      |
| 4      | 19  | 20  | 21   | 22  | 23  | 24  | 25   | 26   | 27  | 28   | 29   | 30   | 31   | 32   | 33   | 34   | 35   | 36   |
|        | K   | Ca  | Sc   | Ti  | V   | Cr  | Mn   | Fe   | Co  | Ni   | Cu   | Zn   | Ga   | Ge   | As   | Se   | Br   | Kr   |
|        | 4s  |     | 3d   |     |     |     |      |      |     |      |      |      | 4p   |      |      |      |      |      |
| 5      | 37  | 38  | 39   | 40  | 41  | 42  | 43   | 44   | 45  | 46   | 47   | 48   | 49   | 50   | 51   | 52   | 53   | 54   |
|        | Rb  | Sr  | Y    | Zr  | Nb  | Mo  | Tc   | Ru   | Rh  | Pd   | Ag   | Cd   | In   | Sn   | Sb   | Te   | I    | Xe   |
|        | 5s  |     | 4d   |     |     |     |      |      |     |      |      |      | 5p   |      |      |      |      |      |
| 6      | 55  | 56  | 57   | 72  | 73  | 74  | 75   | 76   | 77  | 78   | 79   | 80   | 81   | 82   | 83   | 84   | 85   | 86   |
|        | Cs  | Ba  | La   | Hf  | Ta  | W   | Re   | Os   | Os  | Pt   | Au   | Hg   | Tl   | Pb   | Bi   | Po   | At   | Rn   |
|        | 6s  |     | 5d   |     |     |     |      |      |     |      |      |      | 6p   |      |      |      |      |      |
| 7      | 87  | 88  | 89   | 104 | 105 | 106 | 107  | 108  | 109 | 110  | 111  | 112  |      |      |      |      |      |      |
|        | Fr  | Ra  | Ac   | Rf  | Db  | Sg  | Bh   | Hs   | Mt  | Ds   |      |      |      |      |      |      |      |      |
|        | 7s  |     | 6d   |     |     |     |      |      |     |      |      |      |      |      |      |      |      |      |
|        |     |     |      |     |     |     |      |      |     |      |      |      |      |      |      |      |      |      |
| 6      | 58  | 59  | 60   | 61  | 62  | 63  | 64   | 65   | 66  | 67   | 68   | 69   | 70   | 71   |      |      |      |      |
|        | Ce  | Pr  | Nd   | Pm  | Sm  | Eu  | Gd   | Tb   | Dy  | Ho   | Er   | Tm   | Yb   | Lu   |      |      |      |      |
|        | 4f  |     |      |     |     |     |      |      |     |      |      |      |      |      |      |      |      |      |
| 7      | 90  | 91  | 92   | 93  | 94  | 95  | 96   | 97   | 98  | 99   | 100  | 101  | 102  | 103  |      |      |      |      |
|        | Th  | Pa  | U    | Np  | Pu  | Am  | Cm   | Bk   | Cf  | Es   | Fm   | Md   | No   | Lr   |      |      |      |      |
|        | 5f  |     |      |     |     |     |      |      |     |      |      |      |      |      |      |      |      |      |

**Fig. 3.1** A Periodic Table to show the kinds of atomic orbitals (sublevels) being filled, below the symbols of blocks of elements. The electronic structures of the A group and O (VIIIA) group elements are perfectly regular and can be predicted from their positions in the Periodic Table, but there are many exceptions in the *d* and *f* blocks.

Table 3.2 Long Form of Periodic Table

Main-Group Elements

Main-Group Elements

|              |                       |                                                            |                       |                       |                        |                        |                       |                     |                      |                       |                         |                       |                       |                       |                       |                    |                      |  |  |  |  |
|--------------|-----------------------|------------------------------------------------------------|-----------------------|-----------------------|------------------------|------------------------|-----------------------|---------------------|----------------------|-----------------------|-------------------------|-----------------------|-----------------------|-----------------------|-----------------------|--------------------|----------------------|--|--|--|--|
| 1<br>IA      |                       | 1 ← Atomic number<br>H ← Symbol<br>1.00794 ← Atomic weight |                       |                       |                        |                        |                       |                     |                      |                       |                         |                       |                       |                       |                       |                    |                      |  |  |  |  |
| 1            | 1<br>H<br>1.00794     | 2<br>IIA                                                   | Transition Metals     |                       |                        |                        |                       |                     |                      |                       |                         |                       | 13<br>IIIA            | 14<br>IVA             | 15<br>VA              | 16<br>VIA          | 18<br>VIIA           |  |  |  |  |
| 2            | 3<br>Li<br>6.941      | 4<br>Be<br>9.012182                                        |                       |                       |                        |                        |                       |                     |                      |                       |                         |                       | 5<br>B<br>10.811      | 6<br>C<br>12.011      | 7<br>N<br>14.00674    | 8<br>O<br>15.9994  | 9<br>F<br>18.9984032 |  |  |  |  |
| 3            | 11<br>Na<br>22.989768 | 12<br>Mg<br>24.3050                                        | 3<br>IIIB             | 4<br>IVB              | 5<br>VB                | 6<br>VIB               | 7<br>VIIB             | 8                   | 9<br>VIIB            | 10                    | 11<br>IB                | 12<br>IIB             | 13<br>Al<br>26.981539 | 14<br>Si<br>28.0855   | 15<br>P<br>30.973762  | 16<br>S<br>32.066  | 17<br>Cl<br>35.4527  |  |  |  |  |
| 4            | 19<br>K<br>39.0983    | 20<br>Ca<br>40.078                                         | 21<br>Sc<br>44.955910 | 22<br>Ti<br>47.88     | 23<br>V<br>50.9415     | 24<br>Cr<br>51.9961    | 25<br>Mn<br>54.93805  | 26<br>Fe<br>55.847  | 27<br>Co<br>58.93320 | 28<br>Ni<br>58.6934   | 29<br>Cu<br>63.546      | 30<br>Zn<br>65.39     | 31<br>Ga<br>69.723    | 32<br>Ge<br>72.61     | 33<br>As<br>74.92169  | 34<br>Se<br>78.96  | 35<br>Br<br>79.904   |  |  |  |  |
| 5            | 37<br>Rb<br>85.4678   | 38<br>Sr<br>87.62                                          | 39<br>Y<br>88.90585   | 40<br>Zr<br>91.224    | 41<br>Nb<br>92.90638   | 42<br>Mo<br>95.94      | 43<br>Tc<br>(98)      | 44<br>Ru<br>101.07  | 45<br>Rh<br>102.9055 | 46<br>Pd<br>106.42    | 47<br>Ag<br>107.8682    | 48<br>Cd<br>112.411   | 49<br>In<br>114.82    | 50<br>Sn<br>118.710   | 51<br>Sb<br>121.757   | 52<br>Te<br>127.60 | 53<br>I<br>126.90447 |  |  |  |  |
| 6            | 55<br>Cs<br>132.90543 | 56<br>Ba<br>137.327                                        | 57<br>La*<br>138.9055 | 72<br>Hf<br>178.49    | 73<br>Ta<br>180.9479   | 74<br>W<br>183.85      | 75<br>Re<br>186.207   | 76<br>Os<br>190.2   | 77<br>Ir<br>192.22   | 78<br>Pt<br>195.08    | 79<br>Au<br>196.96654   | 80<br>Hg<br>200.59    | 81<br>Tl<br>204.3833  | 82<br>Pb<br>207.2     | 83<br>Bi<br>207.98037 | 84<br>Po<br>(209)  | 85<br>At<br>(210)    |  |  |  |  |
| 7            | 87<br>Fr<br>(223)     | 88<br>Ra<br>(226)                                          | 89<br>Ac**<br>(227)   | 104<br>Rf<br>(261.11) | 105<br>Db<br>(262.114) | 106<br>Sg<br>(263.118) | 107<br>Bh<br>(262.12) | 108<br>Hs<br>(265)  | 109<br>Mt<br>(266)   | 110<br>Ds<br>(269)    | Inner-Transition Metals |                       | 114<br>Uuq            |                       |                       |                    |                      |  |  |  |  |
| *Lanthanides |                       |                                                            | 58<br>Ce<br>140.115   | 59<br>Pr<br>140.90765 | 60<br>Nd<br>144.24     | 61<br>Pm<br>(145)      | 62<br>Sm<br>150.36    | 63<br>Eu<br>151.965 | 64<br>Gd<br>157.25   | 65<br>Tb<br>158.92534 | 66<br>Dy<br>162.50      | 67<br>Ho<br>164.93032 | 68<br>Er<br>167.26    | 69<br>Tm<br>168.93421 | 70<br>Yb<br>173.04    |                    |                      |  |  |  |  |
| **Actinides  |                       |                                                            | 90<br>Th<br>232.0381  | 91<br>Pa<br>(231)     | 92<br>U<br>238.0289    | 93<br>Np<br>(237)      | 94<br>Pu<br>(244)     | 95<br>Am<br>(243)   | 96<br>Cm<br>(247)    | 97<br>Bk<br>(247)     | 98<br>Cf<br>(251)       | 99<br>Es<br>(252)     | 100<br>Fm<br>(257)    | 101<br>Md<br>(258)    | 102<br>No<br>(259)    |                    |                      |  |  |  |  |

## Classification of The Elements in Blocks

In Periodic Table, the elements have been arranged in different **periods** and **groups** based on electronic configuration. Classification of the elements into following **four blocks** is decided by the differentiating electron (last filling electron). Block is that in which orbital differentiating electron goes (Aufbau rule)

- (a) *s*-block element                      (b) *p*-block element  
(c) *d*-block element                      (d) *f*-block element

| Element | Atomic no. | E.C.                                 | Last electron goes into | Block   |
|---------|------------|--------------------------------------|-------------------------|---------|
| Na      | 11         | [Ne] 3s <sup>1</sup>                 | s                       | s-block |
| Al      | 13         | [Ne] 3s <sup>2</sup> 3p <sup>1</sup> | p                       | p-block |
| Sc      | 21         | [Ar] 4s <sup>2</sup> 3d <sup>1</sup> | d                       | d-block |
| Ce      | 58         | [Xe] 6s <sup>2</sup> 4f <sup>2</sup> | f                       | f-block |

Blocks have been represented in Fig. 3.1 and Table 3.3.

### s-Block Elements

If shells up to (*n* - 1) are completely filled and the last electron enters the *s*-orbital of the outermost (*n*th) shell, the elements of this class are called **s-block** elements.

- Thus differentiating electron enters the *ns*-orbital.

- General electronic configuration is  
[inert gas] *ns*<sup>*x*</sup>      (*x* = 1, 2)
- If *x* = 1, elements constitute a group of **alkali metals** placed in **first group** (IA).
- If *x* = 2, elements constitute a group of **alkaline earth metals** placed in **second group** (IIA).
- Alkali metals form **monovalent** cations, alkaline earth metals form **divalent** cations with nearest stable configuration of inert gas.
- Period of the element is the value of *x* (number of shells).

| Group IA<br>(First)<br>alkali<br>metals (A) | Electronic configuration of |                                   |                      | Group IIA<br>(Second)<br>alkaline<br>earth<br>metals (A) |
|---------------------------------------------|-----------------------------|-----------------------------------|----------------------|----------------------------------------------------------|
|                                             | Metal A                     | A <sup>+</sup> or B <sup>2+</sup> | Metal B              |                                                          |
| Li <sub>3</sub>                             | [He] 2s <sup>1</sup>        | [He]                              | [He] 2s <sup>2</sup> | Be <sub>4</sub>                                          |
| Na <sub>11</sub>                            | [Ne] 3s <sup>1</sup>        | [Ne]                              | [Ne] 3s <sup>2</sup> | Mg <sub>12</sub>                                         |
| K <sub>19</sub>                             | [Ar] 4s <sup>1</sup>        | [Ar]                              | [Ar] 4s <sup>2</sup> | Ca <sub>20</sub>                                         |
| Rb <sub>37</sub>                            | [Kr] 5s <sup>1</sup>        | [Kr]                              | [Kr] 5s <sup>2</sup> | Sr <sub>38</sub>                                         |
| Cs <sub>55</sub>                            | [Xe] 6s <sup>1</sup>        | [Xe]                              | [Xe] 6s <sup>2</sup> | Ba <sub>56</sub>                                         |
| Fr <sub>87</sub>                            | [Rn] 7s <sup>1</sup>        | [Rn]                              | [Rn] 7s <sup>2</sup> | Ra <sub>88</sub>                                         |

Table 3.3 The s, p, d and f-Block of the Periodic Table

| Periodic Table of the Elements |                   |          |          |          |           |           |           |           |           |           |           |           |           |           |           |           |                          |                 |          |          |          |                |          |          |          |          |          |          |          |          |          |          |          |
|--------------------------------|-------------------|----------|----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|--------------------------|-----------------|----------|----------|----------|----------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Groups                         |                   |          |          |          |           |           |           |           |           |           |           |           |           |           |           |           |                          |                 |          |          |          |                |          |          |          |          |          |          |          |          |          |          |          |
| IA                             | IIA               | IIIB     |          |          |           |           |           | IVB       | VB        | VIB       | VII B     | VIII      | IB        | IIB       | IIIA      | IVA       | VA                       | VIA             | VIIA     | 0        |          |                |          |          |          |          |          |          |          |          |          |          |          |
| (1)                            | (2)               | (3)      |          |          |           |           |           | (4)       | (5)       | (6)       | (7)       | (8)       | (9)       | (10)      | (11)      | (12)      | (13)                     | (14)            | (15)     | (16)     | (17)     | (18)           |          |          |          |          |          |          |          |          |          |          |          |
| s-orbital block                |                   |          |          |          |           |           |           |           |           |           |           |           |           |           |           |           |                          | p-orbital block |          |          |          | s <sup>2</sup> |          |          |          |          |          |          |          |          |          |          |          |
| s <sup>1</sup>                 |                   |          |          |          |           |           |           |           |           |           |           |           |           |           |           |           |                          |                 |          |          |          | 2<br>He        |          |          |          |          |          |          |          |          |          |          |          |
| n = 1                          | 1<br>H            |          |          |          |           |           |           |           |           |           |           |           |           |           |           |           |                          |                 |          |          |          |                |          |          |          |          |          |          |          |          |          |          |          |
| n = 2                          | 3<br>Li           | 4<br>Be  |          |          |           |           |           |           |           |           |           |           |           |           |           |           |                          | 5<br>B          | 6<br>C   | 7<br>N   | 8<br>O   | 9<br>F         | 10<br>Ne |          |          |          |          |          |          |          |          |          |          |
| n = 3                          | 11<br>Na          | 12<br>Mg |          |          |           |           |           |           |           |           |           |           |           |           |           |           |                          | 13<br>Al        | 14<br>Si | 15<br>P  | 16<br>S  | 17<br>Cl       | 18<br>Ar |          |          |          |          |          |          |          |          |          |          |
| n = 4                          | 19<br>K           | 20<br>Ca | 21<br>Sc |          |           |           |           |           |           |           |           |           |           |           |           |           |                          |                 | 22<br>Ti | 23<br>V  | 24<br>Cr | 25<br>Mn       | 26<br>Fe | 27<br>Co | 28<br>Ni | 29<br>Cu | 30<br>Zn | 31<br>Ga | 32<br>Ge | 33<br>As | 34<br>Se | 35<br>Br | 36<br>Kr |
| n = 5                          | 37<br>Rb          | 38<br>Sr | 39<br>Y  |          |           |           |           |           |           |           |           |           |           |           |           |           |                          |                 | 40<br>Zr | 41<br>Nb | 42<br>Mo | 43<br>Tc       | 44<br>Ru | 45<br>Rh | 46<br>Pd | 47<br>Ag | 48<br>Cd | 49<br>In | 50<br>Sn | 51<br>Sb | 52<br>Te | 53<br>I  | 54<br>Xe |
| n = 6                          | 55<br>Cs          | 56<br>Ba | 57<br>La | 58<br>Ce | 71<br>Lu  | 72<br>Hf  | 73<br>Ta  | 74<br>W   | 75<br>Re  | 76<br>Os  | 77<br>Ir  | 78<br>Pt  | 79<br>Au  | 80<br>Hg  | 81<br>Tl  | 82<br>Pb  | 83<br>Bi                 | 84<br>Po        | 85<br>At | 86<br>Rn |          |                |          |          |          |          |          |          |          |          |          |          |          |
| n = 7                          | 87<br>Fr          | 88<br>Ra | 89<br>Ac | 90<br>Th | 103<br>Lr | 104<br>Rf | 105<br>Db | 106<br>Sg | 107<br>Bh | 108<br>Hs | 109<br>Mt | 110<br>Ds | 111       | 112       |           |           |                          |                 |          |          |          |                |          |          |          |          |          |          |          |          |          |          |          |
| n = 6                          | Lanthanide Series |          | 58<br>Ce | 59<br>Pr | 60<br>Nd  | 61<br>Pm  | 62<br>Sm  | 63<br>Eu  | 64<br>Gd  | 65<br>Tb  | 66<br>Dy  | 67<br>Ho  | 68<br>Er  | 69<br>Tm  | 70<br>Yb  | 71<br>Lu  | 4f subshell being filled |                 |          |          |          |                |          |          |          |          |          |          |          |          |          |          |          |
| n = 7                          | Actinide Series   |          | 90<br>Th | 91<br>Pa | 92<br>U   | 93<br>Np  | 94<br>Pu  | 95<br>Am  | 96<br>Cm  | 97<br>Bk  | 98<br>Cf  | 99<br>Es  | 100<br>Fm | 101<br>Md | 102<br>No | 103<br>Lr | 5f subshell being filled |                 |          |          |          |                |          |          |          |          |          |          |          |          |          |          |          |

\*n is the principal quantum number. The  $d^1s^2, d^2s^2, \dots$  designations represent known configurations. They refer to  $(n-1)d$  and  $ns$  orbitals.

## p-Block Elements

If shells up to  $(n-1)$  are completely filled and differentiating electron enters the  $p$ -orbital of the  $n$ th orbit, elements of this class are called **p-block elements**.

- General E.C. is  $ns^2 np^x$  ( $x = 1$  to  $6$ )
- Group is  $(2+x)$  A based on old system IIIA, IVA, ..... and  $(12+x)$  based on new IUPAC system.
- The  $s$ -block and  $p$ -block elements together are called **representative elements** or **main group elements**.

| Period | Elements    |             |             |             |             |             |
|--------|-------------|-------------|-------------|-------------|-------------|-------------|
| 2      | B           | C           | N           | O           | F           | Ne          |
| 3      | Al          | Si          | P           | S           | Cl          | Ar          |
| 4      | Ga          | Ge          | As          | Se          | Br          | Kr          |
| 5      | In          | Sn          | Sb          | Te          | I           | Xe          |
| 6      | Tl          | Pb          | Bi          | Po          | At          | Rn          |
| E.C.   | $ns^2 np^1$ | $ns^2 np^2$ | $ns^2 np^3$ | $ns^2 np^4$ | $ns^2 np^5$ | $ns^2 np^6$ |
| x      | 1           | 2           | 3           | 4           | 5           | 6           |
| old    | IIIA        | IVA         | VA          | VIA         | VIIA        | VIIIA (0)   |
| new    | 13          | 14          | 15          | 16          | 17          | 18          |

**Illustration 1** Group the following electron configurations in pairs that would represent similar chemical properties of their atoms :

- $1s^2 2s^2 2p^6 3s^2$
- $1s^2 2s^2 2p^3$
- $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$
- $1s^2 2s^2$
- $1s^2 2s^2 2p^6$
- $1s^2 2s^2 2p^6 3s^2 3p^3$

**Solution** If there is repetition of electron configuration (E.C.) of the valence shell, then chemical properties are also repeated. Thus pairs with similar chemical properties are :

### Valence shell EC

- I : (a) and (d) [inert gas]  $ns^2$   
 II : (b) and (f)  $ns^2 np^3$ -nitrogen family of  $p$ -block  
 III : (c) and (e)  $ns^2 np^6$ -inert gas

## d-Block Elements

If outermost ( $n$ th) and penultimate  $[(n-1)\text{th}]$  are incompletely filled and differentiating electron enters the

$(n-1)d$  orbitals (i.e.,  $d$ -orbital of penultimate shell) then elements of this class are called  **$d$ -block** elements.

- $d$ -block elements are placed between  $s$ -block and  $p$ -block elements and thus also called transition elements.

• EC is  $(n-1)d^x ns^y$

where  $x$  = number of electrons in  $(n-1)d$  orbital

$x = 1$  to 10 (except 4 and 9)

$y$  = number of electrons in  $ns$ -orbital.

$y = 2$  in all cases except in groups 6 (VIB) and

11 (IB)  $y = 1$

- IUPAC (new pattern) group =  $(x + y)$  but old group is decided by

— group is  $(x + y)B$  if  $x < 6$

— group is VIII B if  $x = 6, 7, 8$

— group is  $yB$  if  $x = 10$

| Element | Z (atomic number) | EC                  | $x$ | $y$ | Group |        |
|---------|-------------------|---------------------|-----|-----|-------|--------|
|         |                   |                     |     |     | New   | Old    |
| Sc      | 21                | $[Ar] 3d^1 4s^2$    | 1   | 2   | 3     | III B  |
| Ti      | 22                | $[Ar] 3d^2 4s^2$    | 2   | 2   | 4     | IV B   |
| V       | 23                | $[Ar] 3d^3 4s^2$    | 3   | 2   | 5     | V B    |
| Cr      | 24                | $[Ar] 3d^5 4s^1$    | 5   | 1   | 6     | VI B   |
| Mn      | 25                | $[Ar] 3d^5 4s^2$    | 5   | 2   | 7     | VII B  |
| Fe      | 26                | $[Ar] 3d^6 4s^2$    | 6   | 2   | 8     | VIII B |
| Co      | 27                | $[Ar] 3d^7 4s^2$    | 7   | 2   | 9     | VIII B |
| Ni      | 28                | $[Ar] 3d^8 4s^2$    | 8   | 2   | 10    | VIII B |
| Cu      | 29                | $[Ar] 3d^{10} 4s^1$ | 10  | 1   | 11    | I B    |
| Zn      | 30                | $[Ar] 3d^{10} 4s^2$ | 10  | 2   | 12    | II B   |

- $d$ -block elements are further classified into following three transition series on the basis of which  $(n-1)d$  is being filled:

| Series | Elements                                              | $(n-1)d$ being filled |
|--------|-------------------------------------------------------|-----------------------|
| 3d     | Sc <sub>21</sub> —Zn <sub>30</sub>                    | 3d                    |
| 4d     | Y <sub>39</sub> —Cd <sub>48</sub>                     | 4d                    |
| 5d     | La <sub>57</sub> , Hf <sub>72</sub> —Hg <sub>80</sub> | 5d                    |

**Illustration 2** Specify the group of the Periodic Table in which each of the following elements is found?

(a)  $[Ne] 3s^1$       (b)  $[Ne] 3s^2 3p^3$       (c)  $[Ne] 3s^2 3p^6$

(d)  $[Ar] 4s^2 3d^8$

**Solution**

| EC                   | Group       | Element |
|----------------------|-------------|---------|
| (a) $[Ne] 3s^1$      | IA (1)      | Na      |
| (b) $[Ne] 3s^2 3p^3$ | VA (15)     | P       |
| (c) $[Ne] 3s^2 3p^6$ | VIIIA (18)  | Ar      |
| (d) $[Ar] 4s^2 3d^8$ | VIII B (10) | Ni      |

**Illustration 3** A  $M^{2+}$  ion derived from a metal in the first transition metal series has four electrons in  $3d$  subshell. What element might  $M$  be?

**Solution** EC of  $M^{2+}$  :  $[Ar]_{18} 4s^0 3d^4$

$\therefore$  EC of  $M$  :  $[Ar] 4s^1 3d^5$  (and not  $4s^2 3d^4$ )

Total electrons = 24

Hence,  $M$  is Cr.

## f-Block Elements

If  $n$ ,  $(n-1)$  and  $(n-2)$  are incompletely filled and last electron enters into  $f$ -orbital of ante penultimate i.e.,  $(n-2)$  th shell, elements of this class are called  **$f$ -block** elements.

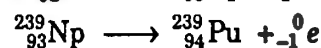
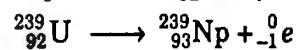
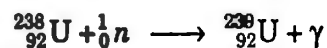
- Thus differentiating electron enters  $(n-2)f$  orbital.
- General E.C. is  $(n-2)f^{2-14}(n-1)d^{0,1}ns^2$
- If  $n=6$ , elements belong to **lanthanides** with E.C.  $4f^{2-14}5d^{0,1}6s^2$  of the elements with atomic number Ce (58) to Lu (71)  
 $Ce_{58} : [Xe]_{54} 4f^2 5d^0 6s^2$        $Gd_{64} : [Xe]_{54} 4f^7 5d^1 6s^2$   
 $Lu_{71} : [Xe]_{54} 4f^{14} 5d^1 6s^2$
- If  $n=7$ , elements belong to **actinides** with E.C.  $5f^{2-14}6d^{0,1}7s^2$  of the elements with atomic number Th (90) to Lr (103).  
 $Th_{90} : [Rn]_{86} 5f^2 6d^0 7s^2$   
 $Cm_{96} : [Rn]_{86} 5f^7 6d^1 7s^2$   
 $Lr_{103} : [Rn]_{86} 5f^{14} 6d^1 7s^2$
- All the elements of  $f$ -block ( $4f$  series—Lanthanides and  $5f$  series—Actinides) are placed in 3rd group (IIIB) and form a separate block at the bottom of the Periodic Table.
- They are also called **inner-transition** elements.

## DEEP Focus

- They were also called **rare-earth elements** since their oxides (earth) were rare in earlier days.

## Nomenclature of the Elements

Elements with atomic numbers greater than 92 (atomic number of uranium) are called the **transuranium** elements. All these elements are man-made through artificial nuclear reactions.



- At present, transuranium elements with atomic numbers up to 110 have been reported.
- Very recently, on August 16, 2003, IUPAC approved the name for the element number 110, as **darmstadtium**, with symbol **Ds**.



- **CNIC (Commission on Nomenclature of Inorganic Chemistry)** appointed by IUPAC in 1994, approved official names for elements with atomic number 104 to 109. With  $Z > 109$ , IUPAC recommended a nomenclature to be followed for naming these elements until their names are officially recognised. This nomenclature is based on the Latin words for the atomic numbers of the elements.
- The names are derived by using roots for the three digits in the atomic number of the element and adding the ending *-ium*. The roots for the numbers are :

| Digit | Name | Abbreviation |
|-------|------|--------------|
| 0     | nil  | n            |
| 1     | un   | u            |
| 2     | bi   | b            |
| 3     | tri  | t            |
| 4     | quad | q            |
| 5     | pent | p            |
| 6     | hex  | h            |
| 7     | sept | s            |
| 8     | oct  | o            |
| 9     | enn  | e            |

Thus element with atomic number 109 will be named as **une** (u for 1, n for 0 and e for 9).

Table 3.4 summarises the names of the elements with atomic number above 100.

Table 3.4 IUPAC Nomenclature of Elements with Atomic Number above 100

| Atomic number | Name           | Symbol | IUPAC official name | IUPAC symbol |
|---------------|----------------|--------|---------------------|--------------|
| 101           | Un-nil-unium   | Unu    | Mendelevium         | Md           |
| 102           | Un-nil-bium    | Unb    | Nobelium            | No           |
| 103           | Un-nil-trium   | Unt    | Lawrencium          | Lr           |
| 104           | Un-nil-quadium | Unq    | Rutherfordium       | Rf           |
| 105           | Un-nil-pentium | Unp    | Dubnium             | Db           |
| 106           | Un-nil-hexium  | Unh    | Seaborgium          | Sg           |
| 107           | Un-nil-septium | Uns    | Bohrium             | Bh           |
| 108           | Un-nil-octium  | Uno    | Hassium             | Hs           |
| 109           | Un-nil-ennium  | Une    | Meitnerium          | Mt           |
| 110           | Un-un-illium   | Uun    | Darmstadtium***     |              |
| 111           | Un-un-unium    | Uuu    | **                  |              |
| 112           | Un-un-bium     | Uub    | **                  |              |
| 113           | Un-un-trium    | Uut    | $\alpha$            |              |
| 114           | Un-un-quadium  | Uuq    | **                  |              |
| 115           | Un-un-pentium  | Uup    | $\alpha$            |              |
| 116           | Un-un-hexium   | Uuh    | *                   |              |
| 117           | Un-un-septium  | Uus    | *                   |              |
| 118           | Un-un-octium   | Uuo    | *                   |              |

\* Elements yet to be discovered,

\*\* IUPAC names yet to be announced.

\*\*\* IUPAC approved the name on August 16, 2003.

$\alpha$  Discovered in 2003.

## Target Practice 1

- What are the blocks of the following?  
(a)  $\text{Sc}^{3+}$  (18e) .....  
(b)  $\text{Na}^+$  (10e) .....  
(c)  $\text{Al}^{3+}$  (10e) .....
- Lanthanides (58-71) have ..... elements.
- In the absence of Aufbau rule, what are the blocks of  
(a) K(19) ..... (b) Sc (21) .....  
(c) Ca(20) .....
- What are atomic numbers of the following elements?  
(a) Uut ..... (b) Uuo .....  
(c) Unt .....
- What are symbols for the following having atomic numbers?  
(a) 117 ..... (b) 115 .....  
(c) 104 .....

## Answers

- Blocks are based on atomic number and not on the number of electrons. Thus,  
(a)  $\text{Sc}^{3+}$  (18e,  $z = 21$ )  $[\text{Ar}] 4s^2 3d^1$  *d*-block  
(b)  $\text{Na}^+$  (10e,  $z = 11$ )  $[\text{Ne}] 3s^1$  *s*-block  
(c)  $\text{Al}^{3+}$  (10e,  $z = 13$ )  $[\text{Ne}] 3s^2 3p^1$  *p*-block
- 14
- If Aufbau rule is not followed, electrons are filled in the available orbitals.  
(a) K(19)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$  *d*-block
- (b) Sc (21)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$  *d*-block  
(c) Ca(20)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$  *d*-block
- (a) Uut 113  
↑↑↑  
1 1 3  
(b) Uuo 118  
(c) Unt 103
- (a) 117 uus (b) 115 uup (c) 104 uuq

## Practice Exercise 1

- If each orbital can take maximum of three electrons (elements), what is the number of elements in  
(a) 2nd period, (b) 4th period?
- By use of electron-configuration, decide the group and period of the following elements with atomic number 13, 35, 56, 78, 65
- (a) If **Aufbau rule** is not taken into account, determine the number of elements in each period.  
(b) Assume total number of 112 elements, then how many periods would be required in the Periodic Table without separate position of lanthanides and actinides?
- What are the groups and periods of the elements with atomic numbers 37 and 56?
- Without writing EC can you decide whether the element is alkali metal or alkaline earth metals of the given two types of elements.
- Without using Aufbau rule which of the following elements would be placed in s-block?  
 $Z = 19, 38, 29$
- If it can happen that each orbital can accommodate 3 electrons (for example EC of Na is  $1s^3 2s^3 2p^5$ ), what is block of the elements with  $Z = 12, 19, 37$  when Aufbau rule  
(i) is also valid, (ii) is not valid?
- What is the most important relationship among elements in the same group in the Periodic Table?
- What would be the atomic number of the as-yet-undiscovered alkaline earth element of period 8?
- What are the blocks if EC in the excited states are :  
(A) :  $1s^2, 2s^2 2p^6, 3s^1 3p^3 3d^2$  (B) :  $1s^2, 2s^1 2p^1$   
(C) :  $1s^2, 2s^1 2p^3$
- The p-block elements show two types of oxidation state due to inert pair effect  
 $n$  (valence electrons)  
 $(n - 2)$   
Also stability of  $n$ th state decreases and that of  $(n - 2)$ th increases as one goes down the group. What are different oxidation states of groups 13, 14, 15 starting from 4th period?  
Also write order of their stabilities.
- Following are the p-block elements:  

|    |    |    |
|----|----|----|
| Ge | As | Se |
| 32 | 33 | 34 |

If each orbital can take maximum of three electrons and in the absence of Aufbau rule, specify the  
(i) block  
(ii) group  
(iii) period of the above elements.
- A neutral atom of a certain element has 15 electrons. Without consulting a Periodic Table, answer the following questions:  
(a) What is ground state electron-configuration?  
(b) How should the element be classified?  
(c) Are the atoms of the element diamagnetic or paramagnetic.
- With reference to the Periodic Table, name  
(a) a halogen element in the fourth period  
(b) an element similar to phosphorus in chemical properties  
(c) the most reactive metal in the fifth period  
(d) an element that has an atomic number smaller than 20 and is similar to strontium.
- Elements A, B, C, D and E have the following electron configurations:  
 $A : 1s^2, 2s^2 2p^1$                        $B : 1s^2, 2s^2 2p^6, 3s^2 3p^1$   
 $C : 1s^2, 2s^2 2p^6, 3s^2 3p^3$             $D : 1s^2, 2s^2 2p^6, 3s^2 3p^5$   
 $E : 1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2$   
 Which among these will belong to the same group in the Periodic Table?
- By definition, d-block elements are those in which  $n$  and  $(n - 1)$  shells are incomplete and last electron is being filled into  $(n - 1)d$ -orbitals. For  
 $Zn(30)$                                        $[Ar]_{18} 3d^{10} 4s^2$   
 $Cd(48)$                                        $[Kr]_{36} 4d^{10} 5s^2$   
 $Hg(80)$                                        $[Xe]_{54} 4f^{14} 5d^{10} 6s^2$   
 You find,  $(n - 1)d$  is completely filled. Are their positions in d-block justified.
- What are the blocks, groups and period of the following iso-electronic ions/species ?  
(a)  $Na^+, Mg^{2+}, Al^{3+}$                       (b)  $O^{2-}, Na^+, Ne$   
(c)  $Fe^{2+}, Mn^+, Cr$
- If Aufbau rule is not followed, what are the blocks of the following elements ?  
(a) K (19)                                      (b) Fe (26)  
(c) Ga (31)                                      (d) Sn (50)
- A metal ion with +3 charge has five electrons in the 3d-subshell. Identify the metal.
- EC of Gd (64) is written as:  
 $[Xe]_{54} 4f^7 5d^1 6s^2$   
 and not as  $[Xe]_{54} 4f^8 6s^2$ . Explain.
- Last electron in Lu(71) goes into 5d, but it is studied in f-block. Explain.
- Match the block of the elements with their atomic number:  

| Z  | Block |
|----|-------|
| 55 | p     |
| 45 | f     |
| 81 | s     |
| 64 | d     |
- Write EC of Cm (96). What is its  
(a) group                                      (b) period  
(c) block and                                      (d) magnetic moment?
- Identify the group, family, and/or other Periodic Table location of each element with the outer electron configuration :  
(a)  $ns^2 np^3$   
(b)  $ns^1$   
(c)  $ns^2 (n - 1) d^{0-2} (n - 2) f^{1-14}$   
(d)  $ns^2 (n - 1) d^{1-10}$

## Answers

1. (a) Total orbitals available in 2nd period :  
 $\left. \begin{array}{l} \text{one in } 2s \\ \text{three in } 2p \end{array} \right\} = 4$  hence, number of elements = 12

- (b) Total orbitals available in 4th period :  
 $\left. \begin{array}{l} \text{one in } 4s \\ \text{five in } 3d \\ \text{three in } 4p \end{array} \right\} = 9$  hence, number of elements = 27

| 2. | Z  | Group       | Period |
|----|----|-------------|--------|
|    | 13 | 13 (IIIA)   | 3      |
|    | 35 | 17 (VIIA)   | 4      |
|    | 56 | 2 (IIA)     | 6      |
|    | 78 | 10 (VIII B) | 6      |
|    | 65 | 3 (IIIB)    | 6      |

3. (a) Each group would be having number of elements =  $2n^2$ , where  $n$  stands for number of period.

| $n$ | Elements |
|-----|----------|
| 1   | 2        |
| 2   | 8        |
| 3   | 18       |
| 4   | 32       |
| 5   | 50       |
| 6   | 72       |
| 7   | 98       |

- (b) Total number of six periods, sixth period having only 2 elements [based on part (a)].

| 4. | Z  | Period | Group   |
|----|----|--------|---------|
|    | 37 | 4th    | IA (1)  |
|    | 56 | 5th    | IIA (2) |

5. Yes : Atomic number of alkali metals is not divisible by 2 while that of alkaline earth metals, it is divisible by 2.

e.g., Na — 11  
Mg — 12

| 6. | Z  | (EC)                                              | Block   |
|----|----|---------------------------------------------------|---------|
|    | 19 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$                   | d-block |
|    | 38 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^2$ | d-block |
|    | 29 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$           | s-block |

| 7. Atomic no. | (EC)                                 |       |                                    |       |
|---------------|--------------------------------------|-------|------------------------------------|-------|
|               | Aufbau rule is valid                 | Block | Aufbau rule is not valid           | Block |
| 12            | $1s^2 2s^2 2p^6$                     | p     | $1s^3 2s^3 2p^6$                   | p     |
| 19            | $1s^3 2s^3 2p^9 3s^3 3p^1$           | p     | $1s^3 2s^3 2p^9 3s^3 3p^1$         | p     |
| 37            | $1s^3 2s^3 2p^9 3s^3 3p^9 4s^3 3d^7$ | d     | $1s^3 2s^3 2p^9 3s^3 3p^9 3d^{10}$ | d     |

8. They have similar valence shell E.C.

9. Atomic number = 120

10. (A) p-block (B) s-block (C) p-block

11. Ga, In, Tl +3, +1  $Ga^+ < In^+ < Tl^+$   
 Ge, Sn, Pb +4, +2  $Ge^{2+} < Sn^{2+} < Pb^{2+}$   
 As, Sb, Bi +5, +3  $As^{3+} < Sb^{3+} < Bi^{3+}, Pb^{2+} > Pb^{4+}, Sn^{2+} < Sn^{4+}$

| 12. | Element          | (EC)                            | Block | Group | Period |
|-----|------------------|---------------------------------|-------|-------|--------|
|     | Ge <sub>32</sub> | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ | d     | 17    | 3      |
|     | As <sub>33</sub> | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ | d     | 18    | 3      |
|     | Se <sub>34</sub> | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$ | d     | 19    | 3      |

13. (a)  $1s^2 2s^2 2p^6 3s^2 3p^3$  (b) p-block, group VA (15), period 3  
 (c) paramagnetic since there are (three) unpaired electrons

14. (a) Br (b) N (C) Rb (d) Mg 15. A and B

16. Zn, Cd, Hg, with  $(n-1)d^{10} ns^2$  electronic configuration can't be considered in d-block due to completely filled  $(n-1)d$  orbital. Although these elements form +2 cations, they do not have much in common with Be, Mg and Ca to Ra group except for some resemblance between Zn, Mg and Be.  
 2(IIA) group elements form +2 cation with inert gas configuration while 12(IIIB) group elements form +2 cation with  $(n-1)d^{10}$  configuration which makes study of these elements in d-block.

17. It is atomic number and not the number of electrons that decide position in the Periodic Table.

| (a) | Ions/species     | Group     | Period | Block |
|-----|------------------|-----------|--------|-------|
|     | Na <sup>+</sup>  | 1(IA)     | 3      | s     |
|     | Mg <sup>2+</sup> | 2(IIA)    | 3      | s     |
|     | Al <sup>3+</sup> | 13(IIIA)  | 3      | p     |
| (b) | O <sup>2-</sup>  | 16(VIA)   | 2      | p     |
|     | Na <sup>+</sup>  | 1(IIA)    | 3      | s     |
|     | Ne               | 18(VIIIA) | 2      | p     |
| (c) | Fe <sup>2+</sup> | 8(VIIIB)  | 4      | d     |
|     | Mn <sup>+</sup>  | 7(VIIB)   | 4      | d     |
|     | Cr               | 6(VIB)    | 4      | d     |

18. In the absence of Aufbau rule, (EC) and last filling electron decides the block

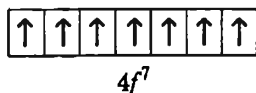
- (i) K<sub>19</sub>  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$   
 (ii) Fe<sub>26</sub>  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$   
 (iii) Ga<sub>31</sub>  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$   
 (iv) Sn<sub>50</sub>  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^4$

|       | Changed block | Original block |
|-------|---------------|----------------|
| (i)   | d             | s              |
| (ii)  | d             | d              |
| (iii) | p             | p              |
| (iv)  | f             | p              |

Thus, block would change in case of K and Sn if EC is written without Aufbau rule.

19. Fe (Z = 26) : [Ar]<sub>18</sub>  $4s^2 3d^6$   
 Fe<sup>3+</sup> : [Ar]<sub>18</sub>  $4s^0 3d^5$

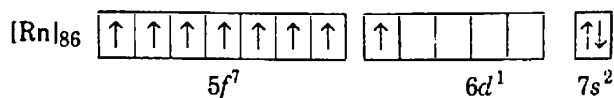
20. In this EC all the electrons in  $4f^7$  are unpaired and thus is stable.



21.  $\text{Lu}_{71}$  is studied in  $f$ -block based on its properties.

| 22. | Z  | Block |
|-----|----|-------|
|     | 55 | s     |
|     | 45 | d     |
|     | 81 | p     |
|     | 64 | f     |

23.  $\text{Cm}(96)$   
EC  $[\text{Rn}]_{86} 5f^7 6d^1 7s^2$



- (a) Group = 3 (IIIB)  
 (b) Period = 7th  
 (c) Block = f  
 (d) Magnetic moment =  $\sqrt{N(N+2)} \text{ BM} = \sqrt{80} \text{ BM}$   
 $N$  = number of unpaired electrons

24. Group Family  
 (a) VA (15) nitrogen  
 (b) IA (1) alkali  
 (c) IIIB (3) inner-transition metals  
 (d) — transition metals

## Periodicity

The recurrence of similar properties of elements after certain regular intervals when they are arranged in the order of increasing atomic number is called **periodicity**.

- Periodicity is due to recurrence of similar outer electronic configurations of their atoms at certain regular intervals. (Table 3.5)
- Recurrence of properties is after 2, 8, 8, 18, 18 and 32 elements (these number are called magic numbers).

Table 3.5 E.C. of Elements of Group 1, 17 and 18

| 1 (Alkali metals) | 17 (Halogen family)  | 18 (Noble gases)     |
|-------------------|----------------------|----------------------|
| Li [He] $2s^1$    | F : $1s^2 2s^2 2p^5$ | He : $1s^2$          |
| Na [Ne] $3s^1$    | Cl : ... $3s^2 3p^5$ | Ne : $2s^2 2p^6$     |
| K [Ar] $4s^1$     | Br : ... $4s^2 4p^5$ | Ar : ... $3s^2 3p^6$ |
| Rb [Kr] $5s^1$    | I : ... $5s^2 5p^5$  | Kr : ... $4s^2 4p^6$ |
| Cs [Xe] $6s^1$    | At : ... $6s^2 6p^5$ | Xe : ... $5s^2 5p^6$ |
| Fr [Rn] $7s^1$    |                      | Rn : ... $6s^2 6p^6$ |

From left to right across a period there is a transition from metals to metalloids to non-metals. Consider the third-period elements from Na to Ar.

### DEEP Focus

- Sodium, the first element in the third period, is a very reactive metal, whereas chlorine, the second-to-last element of that period, is a very reactive non-metal. In between, the elements show a gradual transition from metallic properties to non-metallic properties.
- Na, Mg and Al all have extensive three-dimensional atomic networks, which are held together by forces characteristic of the metallic state.
- Si is a metalloid; it has a giant three-dimensional structure in which the Si atoms are held together very strongly. Starting with phosphorus, the elements exist in simple, discrete molecular units ( $\text{P}_4$ ,  $\text{S}_8$ ,  $\text{Cl}_2$  and Ar) which have low melting points (m.p.) and boiling points (b.p.).

- Within a periodic group the physical properties vary more predictably, especially if the elements are in same physical state. For example, the m.p. of Ar and Xe are  $-189.2^\circ\text{C}$  and  $-111.9^\circ\text{C}$ , respectively. We can estimate the m.p. of the intermediate element (which is Kr) by taking the average of these two values as follows :

$$\begin{aligned} \text{m.p. of Kr} &= \frac{(-189.2) + (-111.9)}{2} \\ &= -150.55^\circ\text{C} \end{aligned}$$

This value is quite close to the actual m.p. of  $-156.6^\circ\text{C}$ .

## Valency and Oxidation Number

Valency and oxidation number of the elements are determined along a group and period.

### Variation in a Group

- For a group, valency is constant.
- Valency =  $N$  if  $N \leq 4$   
 $= (N - 8)$  if  $N \geq 4$

where  $N$  is the number of valence electrons.

|         | 1<br>(IA) | 2<br>(IIA) | 13<br>(IIIA) | 14<br>(IVA) | 15<br>(VA) | 16<br>(VIA) | 17<br>(VIIA) | 18<br>(VIIIA) |
|---------|-----------|------------|--------------|-------------|------------|-------------|--------------|---------------|
|         | Li        | Be         | B            | C           | N          | O           | F            | Ne            |
| Z       | 3         | 4          | 5            | 6           | 7          | 8           | 9            | 10            |
| N       | 1         | 2          | 3            | 4           | 5          | 6           | 7            | 8             |
| valency | 1         | 2          | 3            | 4           | -3         | -2          | -1           | 0             |
|         |           |            |              | -4          |            |             |              |               |

In  $\text{CO}_2$ , C is +4 and in  $\text{CH}_4$ , C is -4.

Due to **Inert-pair effect** (refer *p*-block elements), *p*-block elements in 4th and higher periods have two types of oxidation states/valencies, *N* and (*N* – 2). Stability of higher *N*th state decreases and that of lower (*N* – 2)th state increases going down the group.

| Group     | Element    | <i>N</i> | Oxidation state | Stability order                                                                                              |
|-----------|------------|----------|-----------------|--------------------------------------------------------------------------------------------------------------|
| 13 (IIIA) | Ga, In, Tl | 3        | +1, +3          | $Ga^{3+} > In^{3+} > Tl^{3+}$<br>$Ga^+ < In^+ < Tl^+$<br>$Ga^{3+} > Ga^+$<br>$Tl^{3+} < Tl^+$                |
| 14 (IVA)  | Ge, Sn, Pb | 4        | +2, +4          | $Ge^{4+} > Sn^{4+} > Pb^{4+}$<br>$Ge^{2+} < Sn^{2+} < Pb^{2+}$<br>$Sn^{4+} > Sn^{2+}$<br>$Pb^{4+} < Pb^{2+}$ |
| 15 (VA)   | As, Sb, Bi | 5        | +3, +5          | $As^{5+} > Sb^{5+} > Bi^{5+}$<br>$As^{3+} < Sb^{3+} < Bi^{3+}$<br>$As^{5+} > As^{3+}$<br>$Bi^{5+} < Bi^{3+}$ |

## Variation in Period

- Valency, w.r.t. O (= 2), increases 1 to 7 in a period left to right

|                       | Na                | Mg  | Al                             | Si               | P                             | S               | Cl                             |
|-----------------------|-------------------|-----|--------------------------------|------------------|-------------------------------|-----------------|--------------------------------|
| Compounds with oxygen | Na <sub>2</sub> O | MgO | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | SO <sub>3</sub> | Cl <sub>2</sub> O <sub>7</sub> |
| Valency               | 1                 | 2   | 3                              | 4                | 5                             | 6               | 7                              |

- Valency, w.r.t. H (= 1), increases 1 to 4 and then falls to 1.

|                           | Li  | Be               | B               | C               | N               | O                | F  |
|---------------------------|-----|------------------|-----------------|-----------------|-----------------|------------------|----|
| Compounds with hydrogen   | LiH | BeH <sub>2</sub> | BH <sub>3</sub> | CH <sub>4</sub> | NH <sub>3</sub> | H <sub>2</sub> O | HF |
| Valency (numerical value) | 1   | 2                | 3               | 4               | 3               | 2                | 1  |

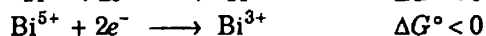
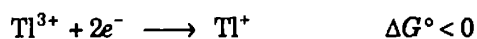
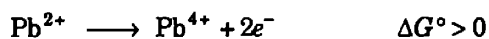
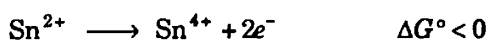
- Inert gases [group 18 (VIIIA)], have zero valency.
- Oxidation states/valencies of the elements have been given in Fig. 3.2.

|                    |                |                |                            |                                 |                            |                                        |                      |                      |                |                      |                |                          |                                            |                            |                                        |                                        |                      |
|--------------------|----------------|----------------|----------------------------|---------------------------------|----------------------------|----------------------------------------|----------------------|----------------------|----------------|----------------------|----------------|--------------------------|--------------------------------------------|----------------------------|----------------------------------------|----------------------------------------|----------------------|
| (1)<br>IA          |                |                |                            |                                 |                            |                                        |                      |                      |                |                      |                |                          |                                            |                            |                                        | (17)<br>VIIA                           | (18)<br>0            |
| 1<br>H<br>+1<br>-1 |                | (2)<br>IIA     |                            |                                 |                            |                                        |                      |                      |                |                      |                |                          |                                            |                            |                                        | 9<br>F<br>-1                           | 2<br>He              |
| 3<br>Li<br>+1      | 4<br>Ba<br>+2  |                |                            |                                 |                            |                                        |                      |                      |                |                      | (13)<br>IIIA   | (14)<br>IVA              | (15)<br>VA                                 | (16)<br>VIA                |                                        | 10<br>Ne                               |                      |
|                    |                |                |                            |                                 |                            |                                        |                      |                      |                |                      | 5<br>B<br>+3   | 6<br>C<br>+4<br>+2<br>-4 | 7<br>N<br>+5<br>+4<br>+3<br>+2<br>+1<br>-3 | 8<br>O<br>-1<br>-2         |                                        |                                        |                      |
| 11<br>Na<br>+1     | 12<br>Mg<br>+2 |                |                            |                                 |                            |                                        |                      |                      |                |                      | 13<br>Al<br>+3 | 14<br>Si<br>+4<br>-4     | 15<br>P<br>+5<br>+3<br>-3                  | 16<br>S<br>+6<br>+4<br>-2  | 17<br>Cl<br>+7<br>+5<br>+3<br>+1<br>-1 | 18<br>Ar                               |                      |
|                    |                | (3)<br>IIIB    | (4)<br>IVB                 | (5)<br>VB                       | (6)<br>VIB                 | (7)<br>VIIB                            | (8)<br>Groups        | (9)<br>VIIIB         | (10)           | (11)<br>IB           | (12)<br>IIB    |                          |                                            |                            |                                        |                                        |                      |
| 19<br>K<br>+1      | 20<br>Ca<br>+2 | 21<br>Sc<br>+3 | 22<br>Ti<br>+4<br>+3<br>+2 | 23<br>V<br>+5<br>+4<br>+3<br>+2 | 24<br>Cr<br>+6<br>+3<br>+2 | 25<br>Mn<br>+7<br>+6<br>+4<br>+3<br>+2 | 26<br>Fe<br>+3<br>+2 | 27<br>Co<br>+3<br>+2 | 28<br>Ni<br>+2 | 29<br>Cu<br>+2<br>+1 | 30<br>Zn<br>+2 | 31<br>Ga<br>+3           | 32<br>Ge<br>+4<br>-4                       | 33<br>As<br>+5<br>+3<br>-3 | 34<br>Se<br>+6<br>+4<br>-2             | 35<br>Br<br>+7<br>+5<br>+3<br>+1<br>-1 | 36<br>Kr<br>+4<br>+2 |

Fig. 3.2 Some non-zero oxidation states (number)

**DEEP Focus**

Based on stability

(Note : If  $\Delta G^\circ$  is negative, reaction is spontaneous)**Shielding (Screening) Effect and Effective Nuclear Charge**

A valence-electron in a multi-electron atom is attracted by the nucleus and repelled by the electrons of inner-shells. The combined effect of this attractive and repulsive force acting on the valence-electron is that the valence-electron experiences less attraction from the nucleus. This is called **shielding** or **screening effect**.

**DEEP Focus**

- According to J.C. Slater, effective nuclear charge  $Z^*$  due to screening is not the actual charge  $Z$  of the nucleus of the atom, but depends on the type of orbital in which the electron is housed, and on the ability of the other electrons in more penetrating orbitals to screen (or shield) the electron in question from the nucleus.
- The relative extent to which the various orbitals penetrate the electron clouds of other orbitals is  $s > p > d > f$ . Thus, for any given principal quantum number  $n$ , an electron will experience the greatest effective nuclear charge when in an  $s$ -orbital, than a  $p$ -orbital and so on.
- The electron is more stable in the more penetrating orbital.

Effective nuclear charge  $Z^*$  due to screening is given by

$$Z^* = Z - \sigma$$

where  $Z$  is the atomic number and  $\sigma$  Slater's screening constant. Values of  $\sigma$  are given below for various types of orbitals. In all cases  $0 < \sigma < Z$ .

| Electrons in orbitals ↓<br>(of shell) → | σ per electron of orbit |         |                   |
|-----------------------------------------|-------------------------|---------|-------------------|
|                                         | $n$                     | $(n-1)$ | $(n-2), (n-3)...$ |
| $s$ -or $p$ -orbital                    | 0.35                    | 0.85    | 1.00              |
| $d$ -or $f$ -orbital                    | 0.35                    | 1.00*   | 1.00              |

\*for all groups on left, including  $s$  or  $p$ -electrons of the same  $n$ .

- For  $1s$  electron,  $\sigma = 0.30$  (in case of two-electron system)

- For H-atom ( $Z = 1$ ), there is no screening, being one-electron system. Thus

$$\sigma = 0 \quad \text{and} \quad Z^* = Z = 1$$

- For He-atom ( $Z = 2$ ),  $1s^2$ , there is screening by one electron on the other electron.

$$\sigma = 0.30 \text{ (of } 1s \text{ electron)}$$

$$\therefore Z^* = 2 - 0.30 = 1.70$$

- For Li-atom, there is screening of outermost electron by 2 electrons in  $1s$  orbit,  $(n-1)$ .

$$\text{Thus } \sigma \text{ for two electrons in } (n-1) = 2 \times 0.85 = 1.70$$

$$\therefore Z^* = 3 - 1.70 = 1.3$$

**DEEP Focus**

- In all cases, screening by  $(Z-1)$  electrons is to be considered.
- One electron system will have  $\sigma = 0$  and thus  $Z^* = Z$ .

Thus in case of H, He<sup>+</sup>, Li<sup>2+</sup>, Be<sup>3+</sup> ... with one electron  $Z^*$  is equal to atomic number.

**In a Period**

| Element | $Z$ | Value of $\sigma$ for $(Z-1)$ electrons in |                 |       | $Z^* = Z - \sigma$ |
|---------|-----|--------------------------------------------|-----------------|-------|--------------------|
|         |     | 1st orbit                                  | 2nd orbit       | Total |                    |
| Li      | 3   | $2 \times 0.85$                            |                 | 1.70  | 1.30               |
| Be      | 4   | $2 \times 0.85$                            | $1 \times 0.35$ | 2.05  | 1.95               |
| B       | 5   | $2 \times 0.85$                            | $2 \times 0.35$ | 2.40  | 2.60               |
| C       | 6   | $2 \times 0.85$                            | $3 \times 0.35$ | 2.75  | 3.25               |
| N       | 7   | $2 \times 0.85$                            | $4 \times 0.35$ | 3.10  | 3.90               |
| O       | 8   | $2 \times 0.85$                            | $5 \times 0.35$ | 3.45  | 4.55               |
| F       | 9   | $2 \times 0.85$                            | $6 \times 0.35$ | 3.80  | 5.20               |
| Ne      | 10  | $2 \times 0.85$                            | $7 \times 0.35$ | 4.15  | 5.85               |

Thus, in a period (left to right), value of  $Z^*$  increases with an increment being of 0.65 per element.

**DEEP Focus**

For second period with  $n$  valence electron

$$Z^* = 0.65[1 + n]$$

For third period with  $n$  valence electron

$$Z^* = 1.55 + 0.65n$$

- For higher periods with  $d$ - and  $f$ -orbitals, variation in  $Z^*$  will differ.

### • In a Group

| Element | Z  | n | Value of $\sigma$ for (Z - 1) electrons in orbit |         |         |         |         |         |         | Total | $Z^* = Z - \sigma$ |
|---------|----|---|--------------------------------------------------|---------|---------|---------|---------|---------|---------|-------|--------------------|
|         |    |   | n                                                | (n - 1) | (n - 2) | (n - 3) | (n - 4) | (n - 5) | (n - 6) |       |                    |
| Li      | 3  | 2 | 0                                                | 1.70    | —       | —       | —       | —       | —       | 1.70  | 1.30               |
| Na      | 11 | 3 | 0                                                | 6.80    | 2.00    | —       | —       | —       | —       | 8.8   | 2.20               |
| K       | 19 | 4 | 0                                                | 6.80    | 8.00    | 2.00    | —       | —       | —       | 16.8  | 2.20               |
| Rb      | 37 | 5 | 0                                                | 6.80    | 8.00    | 18.00   | 2.00    | —       | —       | 34.8  | 2.20               |
| Cs      | 55 | 6 | 0                                                | 6.80    | 18.00   | 18.00   | 8.00    | 2.00    | —       | 52.8  | 2.20               |
| Fr      | 87 | 7 | 0                                                | 6.80    | 32.00   | 18.00   | 18.00   | 8.00    | 2.00    | 84.8  | 2.20               |

- Electron in  $n$ th orbit is screened by electrons in inner-shells, hence  $\sigma = 0$  for electrons in  $n$ th orbit in the above case.

For Kr,  $Z = 36$ ,  $[\text{Ar}] 4s^2 3d^{10} 4p^6$ , electron of highest energy is in  $4p$ ,  $n = 4$

$$Z_{\text{eff}} = \sqrt{\frac{(1350.7)(16)}{1312}} = 4.06$$

### DEEP Focus

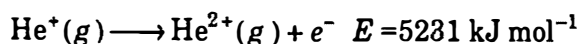
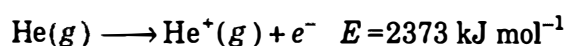
- We find amazing effective nuclear charge in a group. Except for Li (2nd period) all other elements have constant value of  $Z^*$  (2.2 in case of alkali metals). Thus while studying variation of any property in a group, not  $Z$  but principal quantum number,  $n$  will be the deciding factor. As we shall see in the coming sections, variation of radius in a group

$$r_n = \frac{n^2 a_0}{Z} \quad (a_0 = \text{Bohr's radius})$$

will be decided by  $n$  and not by  $Z$  (that will be actually  $Z^*$  and which we have seen is constant).

Thus while studying periodicity in a group, do not consider effect of  $Z$ .

- One way to illustrate electron shielding is to consider the amount of energy required to remove the two electrons from the helium atom.



The reason it takes so much more energy to remove the second electron is that with only one electron present, there is no shielding, and the electron feels the full effect of the +2 nuclear charge.

**Illustration 1** One method for calculating  $Z_{\text{eff}}$  is to use the equation :

$$Z_{\text{eff}} = \sqrt{\frac{(E)(n^2)}{1312 \text{ kJ/mol}}}$$

where  $E$  is the energy necessary to remove an electron from an atom and  $n$  is the principal quantum number of the electron. Use this equation to calculate  $Z_{\text{eff}}$  values for the highest-energy electron in potassium ( $E = 418.8 \text{ kJ mol}^{-1}$ ) and krypton ( $E = 1350.7 \text{ kJ mol}^{-1}$ ).

**Solution** For K,  $Z = 19$   $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1$

$4s^1$  is the electron of highest energy,  $n = 4$

$$Z_{\text{eff}} = \sqrt{\frac{(418.8)(4^2)}{1312}} = 2.26$$

## Size of an Atom and Ion

Atomic radius is taken as the distance from the centre of the nucleus to the outermost shell of the electrons.

- Based on probability concept, an atom does not have well defined boundary. Probability of finding the electron is never zero even at large distance from the nucleus. Hence, exact value of the atomic radius can't be evaluated. Atomic radius is taken as the **effective size** which is the distance of the closest approach of one atom to another atom in a given bonding situation.

- Atomic radius can be

– **Covalent radius** : It is one-half of the distance between the centres of two nuclei (of like atoms) bonded by a single covalent bond.

For atoms known to form single bonds in their elemental state, the experimental bond length may be halved to obtain the respective covalent radius. For example

| Element         | Bond length (pm) | Atomic radius (pm) |
|-----------------|------------------|--------------------|
| H <sub>2</sub>  | 74               | 37*                |
| F <sub>2</sub>  | 142              | 71*                |
| Cl <sub>2</sub> | 199              | 99                 |
| C (diamond)     | 154              | 77                 |

\*Accepted values are H : 29 pm; F : 64 pm.

Atomic radii of elements which do not form single bonds (in their elemental form) may be calculated from observed single bond lengths in compounds with other elements of known atomic radii.

The set of covalent radii obtained in the manner fit experimental bond lengths quite satisfactorily, as may be observed from following table for the halides of carbon, silicon and germanium. The experimental bond lengths (in pm) given in parenthesis show fair agreement (without ten per cent) except some fluorides. The atomic radius of fluorine has been taken as 64 pm because this value fits more closely with experimental data on a large number of fluorine compounds. The correction is empirical in nature.

Similarly, the radius of the hydrogen atom is taken to be 29 pm. These adjusted values for some elements are shown below :

| Molecule         | M=C       | M=Si      | M=Ge      |
|------------------|-----------|-----------|-----------|
| MF <sub>4</sub>  | 141 (148) | 181 (154) | 186 (167) |
| MCl <sub>4</sub> | 176 (176) | 216 (201) | 221 (208) |
| MBr <sub>4</sub> | 191 (191) | 231 (215) | 236 (231) |
| M <sub>4</sub>   | 210 (211) | 250 (243) | 255 (250) |

### Covalent atomic radii (single bond), pm

|   |    |    |     |    |     |    |     |    |     |    |     |    |     |
|---|----|----|-----|----|-----|----|-----|----|-----|----|-----|----|-----|
| H | 29 | Be | 89  | B  | 80  | C  | 77  | N  | 70  | O  | 66  | F  | 64  |
|   |    |    |     | Al | 126 | Si | 117 | P  | 110 | S  | 104 | Cl | 99  |
|   |    | Zn | 131 | Ga | 126 | Ge | 122 | As | 121 | Se | 117 | Br | 114 |
|   |    | Cd | 148 | In | 144 | Sn | 140 | Sb | 141 | Te | 137 | I  | 113 |
|   |    | Hg | 148 | Tl | 147 | Pb | 146 | Bi | 151 |    |     |    |     |

In a heteronuclear, diatomic molecule of AB type, if the bonding is purely covalent, then the bond length  $r_{A-B}$  is equal to the sum of the covalent radii of A and B, i.e.,

$$r_{A-B} = r_A + r_B$$

Thus, covalent radii are additive. Thus known the value of  $r_{A-B}$  and  $r_A$  (or  $r_B$ ), value of  $r_B$  (or  $r_A$ ) can be calculated. If there is difference in the electronegativities of the bonded atoms, it causes shortening of the bonds. Schomaker and Stevenson gave following relation to calculate internuclear distance of the molecule AB with different electronegativity  $X_A$  and  $X_B$  of atom A and B respectively.

$$r_{A-B} = r_A + r_B - 0.07(X_A - X_B)^2$$

### DEEP Focus

Multiplicity of the bond also causes a shortening of the bond. Usually a double bond is about 0.86 times and a triple bond about 0.78 times the single bond length for the second period elements.

One important contribution is likely to come from the attraction between the opposite partial charge built up on the atoms due to their electronegativity difference. The gradual decrease in C—F bond length with increasing substitution by fluorine in the following compounds supports this view.

| Compound                       | C—F distance (pm) |
|--------------------------------|-------------------|
| CH <sub>3</sub> F              | 139.1             |
| CH <sub>2</sub> F <sub>2</sub> | 135.8             |
| CHF <sub>3</sub>               | 133.2             |
| CF <sub>4</sub>                | 132               |

When two atoms are joined by multiple bonds, the bond length is shorter than the sum of their single bond covalent radii. From the observed bond-lengths, it is possible to assign "double bond radii" or "triple bond radii"

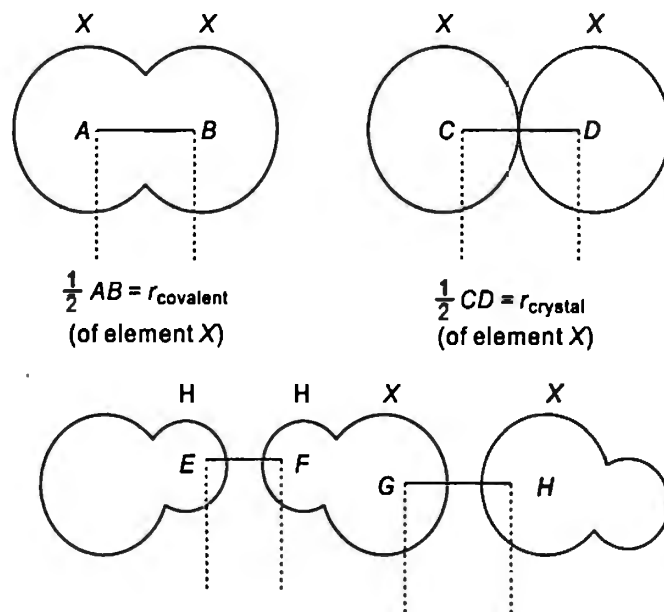
to the atoms. Thus the carbon-carbon bond length of 135 pm in ethylene leads to a double bond radius of carbon equal to 67 pm. Some typical values are given below.

|                    | B  | C  | N  | O  |
|--------------------|----|----|----|----|
| Double bond radius | 71 | 67 | 62 | 62 |
| Triple bond radius | 64 | 60 | 55 |    |

The periodic variation in covalent radii of atoms follows the same trend as the atomic volume. The radii decrease from left to right along a period with increase in nuclear charge. The size should also increase downward along any group with increasing principal quantum number of the outermost shell.

– **van der Waals' radius** : It is one-half of the internucleus distance between two adjacent atoms in two nearest neighbouring molecules of the substance in solid state.

This is obtained from the shortest distance to which two non-bonded atoms can approach before repulsion between their electron clouds come into play.



$$\frac{1}{2} EF = r_{\text{van der Waals}} \text{ of hydrogen in HX molecule}$$

$$\frac{1}{2} GH = r_{\text{van der Waals}} \text{ of X in HX molecule.}$$

$$r_{\text{covalent}} < r_{\text{crystal}} < r_{\text{van der Waals}}$$

– **Crystal radius** : It is one-half of the distance between the nuclei of two adjacent metal atoms in the metallic closed packed crystal lattice.

• Atomic radius/ionic radius in the  $n$ th orbit is given by

$$r_n = \frac{n^2 a_0}{Z^*}$$

where  $n$  is principal quantum number (i.e., number of shell),  $a_0$  the Bohr's radius of H-atom ( $= 0.529 \text{ \AA}$ ) and  $Z^*$ , the effective nuclear charge.

Radius is also dependent on the extent of force of attraction which pulls outer shell inward.



## Variation in a Period

|                          | Li   | Be   | B    | C    | N    | O    | F    | Ne                     |
|--------------------------|------|------|------|------|------|------|------|------------------------|
| $Z$                      | 3    | 4    | 5    | 6    | 7    | 8    | 9    | 10                     |
| $Z^*$                    | 1.30 | 1.95 | 2.60 | 3.25 | 3.90 | 4.55 | 5.20 | 5.85                   |
| $n$                      | 2    | 2    | 2    | 2    | 2    | 2    | 2    | 2                      |
| $r_n$ (pm)<br>(covalent) | 123  | 90   | 80   | 77   | 75   | 74   | 72   | 160 ← (van der Waals') |

**In a period left to right :**

- $Z$  (atomic number) increases (by one unit)
- $Z^*$  (effective nuclear charge due to screening) also increases (but by 0.65 unit)
- $n$  (number of shells) remains constant
- Electrons are pulled close to the nucleus by the increased  $Z^*$ .

Thus, 
$$r_n \propto \frac{1}{Z^*}$$

### DEEP Focus

Thus atomic radii decrease with increase in atomic number in a period left to right. In case of Noble gases (as in Ne) there is no covalent bond formation, hence, only van der Waals' radius is considered. Thus there is high jump in the value of radius from F (72 pm) to Ne (160 pm).

On going across the third period from Na to Ar, for example, each additional electron adds to the same shell (from  $3s^1$  for Na to  $3s^2 3p^6$  for Ar). Because electrons in the same shell are at approximately the same distance from the nucleus, they are relatively ineffective at shielding one another. At the same time, though, the nuclear charge  $Z$  increases from +11 for Na to +18 for Ar. Thus, the effective nuclear charge for the valence-shell electrons increases across the period from 2.20 for Na to 6.75 for Ar, drawing all the valence-shell electrons closer to the nucleus and shrinking the atomic radii (Fig. 3.3).

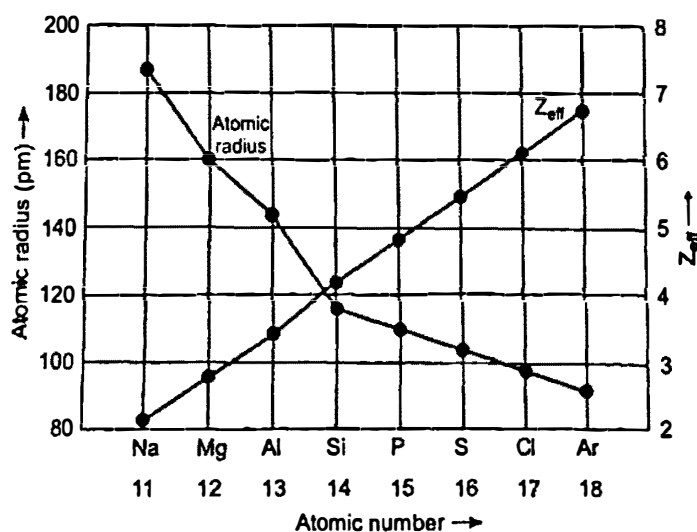


**Fig. 3.3** A plot of both atomic radius and  $Z_{eff}$  for the valence-shell electrons versus atomic number. As  $Z_{eff}$  increases, the valence-shell electrons are attracted more strongly to the nucleus, and the atomic radius therefore decreases.

## Variation in a Group

We consider 1st group (alkali metals) elements :

| Element | $Z$       | $Z^*$    | $n$       | Radius (pm) |
|---------|-----------|----------|-----------|-------------|
| Li      | 3         | 1.3      | 2         | 123         |
| Na      | 11        | 2.2      | 3         | 157         |
| K       | 19        | 2.2      | 4         | 203         |
| Rb      | 37        | 2.2      | 5         | 216         |
| Cs      | 55        | 2.2      | 6         | 235         |
| Fr      | 87        | 2.2      | 7         | —           |
|         | increases | constant | increases | increases   |

### DEEP Focus

In a group, top to bottom,

- $Z$  increases
- but  $Z^*$  (effective nuclear charge due to screening) almost remains constant
- $n$  increases

Since  $r_n \propto \frac{n^2}{Z^*}$ , hence  $r_n \propto n^2$  ( $Z^*$  remaining constant) thus

$r_n$  increases moving along a group top to bottom.

Fig. 3.4 gives the variation of covalent radii of the elements (H to K). In the case of the noble gases, van der Waals' radii have been plotted.

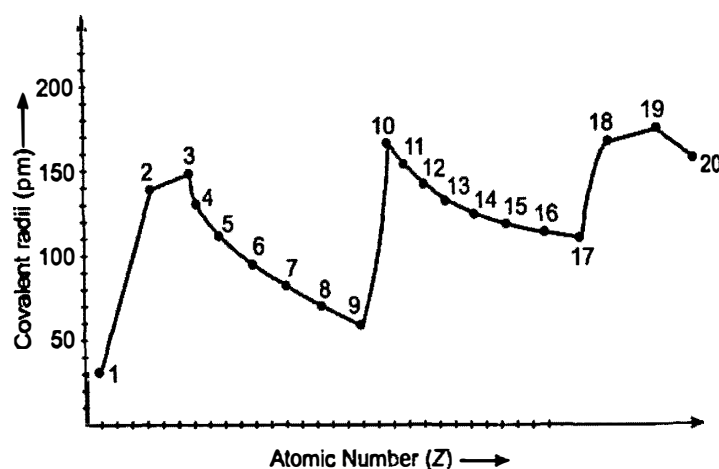
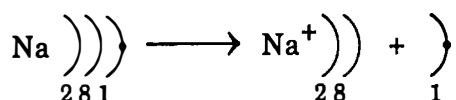


**Fig. 3.4** Covalent radii of first 20 elements.

## Ionic Radius

The effective distance from the nucleus of the ion up to which it has an influence in the ionic bond is called ionic radius.

- **Metal ions (positive ions) are smaller than the atoms from which they were formed due to two factors :**
  - (i) The whole of the outer shell of electrons is usually removed.
  - (ii) In an atom, the number of positive charges on the nucleus is exactly the same as the number of orbital electrons.

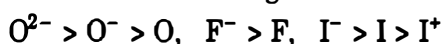


When a positive ion is formed, the number of positive charges on the nucleus exceeds the number of orbital electrons, and the effective nuclear charge is increased. This results in the remaining electrons being more strongly attracted by the nucleus. These electrons are pulled in further reducing the size. **A positive ion is thus always smaller than the corresponding atom and the more electrons which are removed (that is greater the charge on the ion), the smaller the ion becomes.**

Thus,  $\text{Mg} > \text{Mg}^+ > \text{Mg}^{2+}$   
 $\text{Fe} > \text{Fe}^{2+} > \text{Fe}^{3+}$

- **The negative ion is always larger than that of the corresponding atom.** This is due to :

- negative ion is formed by gain of one or more electrons in the neutral atom and thus number of electrons increases but magnitude of nuclear charge remains the same.
- nuclear charge per electron is thus reduced and the electron cloud is held less tightly by the nucleus resulting in the expansion of the outer-shell. Thus size of negative ion is increased.



- The expansion, that occurs when a group 17 (VIIA, halogen) atom gains an electron to form an anion, can be explained by the change in the quantum number of the valence shell since the added electron simply completes an already occupied  $p$ -subshell  $[\text{Ne}] : 3s^2 3p^5$  for a Cl atom to  $[\text{Ne}] 3s^2 3p^6$  for  $\text{Cl}^-$  anion. Thus, the expansion is due entirely to a decrease in effective nuclear charge and to an increase in electron-electron repulsion that occurs when an extra electron is added.
- *Iso-electronic species* (containing equal number of electrons) will have different size due to different values of  $Z$ . Thus,  $\text{N}^{3-}$ ,  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$  (each having 10e) are *iso-electronic* but their radii differ and  $\propto \frac{1}{Z}$ .

|                  | $Z$ | Electron | $e/Z$ |
|------------------|-----|----------|-------|
| $\text{N}^{3-}$  | 7   | 10       | 1.43  |
| $\text{O}^{2-}$  | 8   | 10       | 1.25  |
| $\text{F}^-$     | 9   | 10       | 1.11  |
| $\text{Na}^+$    | 11  | 10       | 0.91  |
| $\text{Mg}^{2+}$ | 12  | 10       | 0.83  |
| $\text{Al}^{3+}$ | 13  | 10       | 0.77  |
| $\text{Si}^{4+}$ | 14  | 10       | 0.71  |

Thus, greater the value of  $(e/Z)$ , greater the size of *iso-electronic species*.

- In the main groups, radii increase on descending the group because extra shell is added.

|               |               |              |
|---------------|---------------|--------------|
| $\text{Li}^+$ | $\text{Na}^+$ | $\text{K}^+$ |
| 76 pm         | 102 pm        | 138 pm       |

- The ionic radii decrease moving from left to right across any period in the Periodic Table.

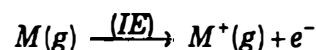
|               |                  |                  |
|---------------|------------------|------------------|
| $\text{Na}^+$ | $\text{Mg}^{2+}$ | $\text{Al}^{3+}$ |
| 102 pm        | 72 pm            | 53.5 pm          |

### DEEP Focus

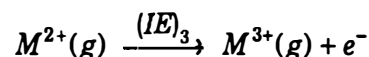
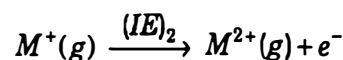
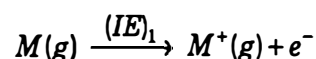
The  $d$  and  $f$ -orbital do not shield the nuclear charge very effectively. Thus there is significant reduction in the size of the ions just after  $d$  or  $f$ -orbitals have been filled completely. This is called **lanthanide contraction** (refer  $d$ -block elements). Zr (160 pm) and Hf (159 pm) thus have equal size due to lanthanide contraction.

## Ionisation Energy

- Ionisation energy ( $IE$ ), sometimes also called **ionisation potential ( $IP$ )**, of an element is defined as the amount of energy required to remove an electron from an isolated gaseous atom of that element resulting in the formation of positive ion.



- ( $IE$ ) is thus a direct measure of the ease with which an atom can change into cation. The smaller the ionisation energy, the easier it is for the neutral atom to change into a positive ion.
- ( $IE$ )<sub>1</sub>, ( $IE$ )<sub>2</sub>, ( $IE$ )<sub>3</sub>... are respectively first, second, third, ... ionisation energies required to remove first, second, third, ... electron from the isolated gaseous atoms.



Thus, second ionisation energy, ( $IE$ )<sub>2</sub>, causes ionisation of  $M^+(g)$  to form  $M^{2+}(g)$  and third ionisation energy, ( $IE$ )<sub>3</sub> causes ionisation of  $M^{2+}(g)$  to form  $M^{3+}(g)$  and so on ...

- ( $IE$ )<sub>3</sub> is also called first ionisation energy of  $M^{2+}(g)$  and second ionisation energy of  $M^+(g)$ . ( $IE$ )<sub>2</sub> is also called first ionisation energy of  $M^+(g)$ .
- **If an electron has been removed from an atom, it becomes increasingly difficult to remove the second and subsequent electrons from the resulting positively charged ions on account of electrostatic attraction. This is due to the fact that after the removal of an electron, the number of electrons decreases while the nuclear charge remains the same. Consequently, the remaining electrons are held**

more tightly by the nucleus and it becomes difficult to remove second electron. Similarly it is further difficult to remove electron from  $M^{2+}(g)$ . Thus

$$(IE)_1 < (IE)_2 < (IE)_3 < \dots$$

Note :  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ ,  $1 \text{ J} = 6.242 \times 10^{18} \text{ eV}$

Successive ionisation energies ( $\text{kJ mol}^{-1}$ ) of some elements are given below :

| Element | Electronic configuration | $(IE)_1$ | $(IE)_2$ | $(IE)_3$ |
|---------|--------------------------|----------|----------|----------|
| Li      | $1s^2 2s^1$              | 520.1    | 7297     | 11810    |
| Be      | $1s^2 2s^2$              | 899.3    | 1758     | 14810    |
| B       | $1s^2 2s^2 2p^1$         | 800.6    | 2428     | 25026    |
| C       | $1s^2 2s^2 2p^2$         | 1086.2   | 2353     | 4618     |
| N       | $1s^2 2s^2 2p^3$         | 1402.1   | 2855     | 4577     |
| O       | $1s^2 2s^2 2p^4$         | 1313.7   | 3388     | 5297     |
| F       | $1s^2 2s^2 2p^5$         | 1680.8   | 3375     | 6045     |
| Ne      | $1s^2 2s^2 2p^6$         | 2080.4   | 3963     | 6130     |

## Factors Influencing Ionisation Energy

( $IE$ ) variation in a period and group may or may not be regular and can be influenced by :

### (1) Size of the Atom

In a small atom, the electrons are tightly held, while in a larger atom, the electrons are less strongly held, the Coulombic force of attraction  $F$  being

$$F = \frac{kZe^2}{r^2}$$

where  $Ze$  is charge on nucleus,  $e$  the electronic charge,  $r$  the atomic size and  $k$  the constant.

Thus, the ionisation energy decreases as the size of the atom increases.

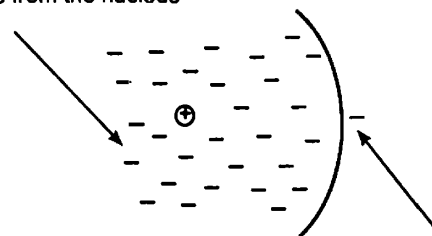
### (2) Nuclear Charge

As given above, the force of attraction between the nucleus and the outermost electron increases with increase in nuclear charge. Greater the nuclear charge, greater the energy required to pull the electron from the atom. Here ( $IE$ ) increases with increase in nuclear charge.

### (3) Shielding Effect

The electrons in the inner-shells act as a screen or shield between the nucleus and the electron in the outermost-shell. This is called **shielding** or **screening** effect. The larger the number of electrons in the inner-shells, greater is the screening effect and smaller the force of attraction and thus ( $IE$ ) decreases.

These electrons shield the outer electrons from the nucleus



This electron does not feel the full effect of the positive charge of the nucleus

Shielding is most effective whenever there is a full shell (or shells) of electrons between the outermost electron and the nucleus, as in case of noble gases (group VIII A). Hence, there is a sharp decrease in ( $IE$ ) going from noble gas to alkali metals as given below:

|      |   |                         |     |      |     |      |     |   |
|------|---|-------------------------|-----|------|-----|------|-----|---|
| He   | → | Li                      | Ne  | →    | Na  | Ar   | →   | K |
| $IE$ |   | 2372                    | 520 | 2081 | 513 | 1521 | 419 |   |
|      |   | (kJ mol <sup>-1</sup> ) |     |      |     |      |     |   |

The shielding is not so important across a period as it is down a group. One reason is that an electron in, say, a  $p_x$  orbital has little shielding effect on an electron in a  $p_y$  or  $p_z$  orbital ( $p_x$ ,  $p_y$  and  $p_z$  are mutually at right angles to one another hence less shielding).  $s$ -orbitals are spherically symmetrical, hence filling of  $1s$  or  $2s$  will experience shielding effect. This comparison is shown in Fig. 3.5.

### (4) Penetration Effect

The ionisation energy also depends on the type of electron which is removed.  $s$ ,  $p$ ,  $d$ , and  $f$ -electrons have orbitals with different shape. An  $s$ -electron penetrates nearer to the nucleus, and is therefore more tightly held than a  $d$ -electron, and a  $d$  electron is more tightly held than an  $f$ -electron. Other factors being equal, ionisation energies are in the order  $s > p > d > f$ . Thus, the increase in ( $IE$ ) is not quite smooth on moving from left to right in the Periodic Table. ( $IE$ )<sub>1</sub> of group 13 (III A) elements (where a  $p$ -electron is being removed) is actually less than adjacent group 2 (IIA) (where an  $s$ -electron is being removed). Also refer Fig. 3.5.

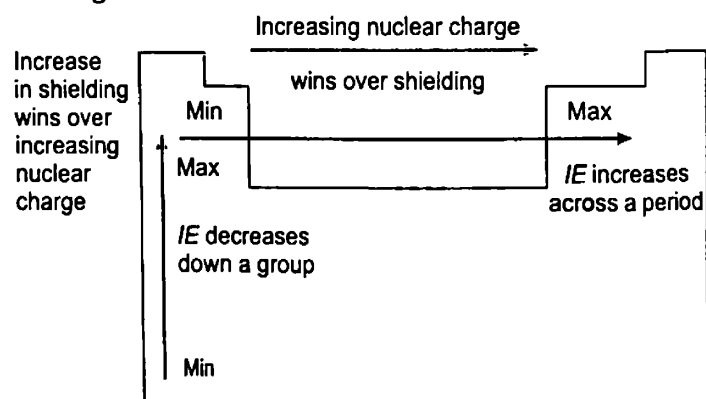
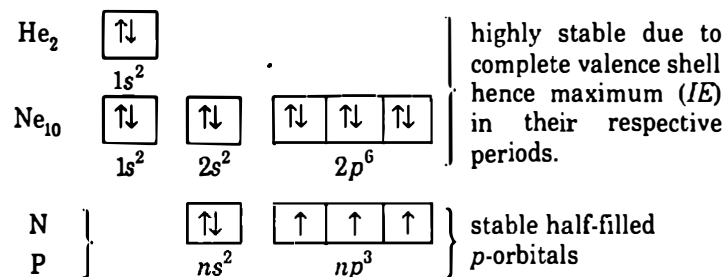


Fig. 3.5 Comparison of shielding effect across a period and a group

## (5) Electronic Configuration

If an atom has fully-filled or half-filled orbitals, its  $(IE)$  is higher than expected normally from its position in the Periodic Table.



## Variation of $(IE)$ in a Group

On moving down a group :

- nuclear charge increases
- $Z^*$  (effective nuclear charge) due to screening is almost constant.
- number of shells increases, hence atomic size increases.
- there is increase in the number of inner electrons which shield the valence electrons from the nucleus.

Thus, force of attraction between electrons and nucleus decreases and tendency to remove the valence electron increases. Hence  $(IE)$  decreases on moving down the group. Variations of  $(IE)_1$  of alkali metals (group I) and boron family (group 13) are given in Fig. 3.6.

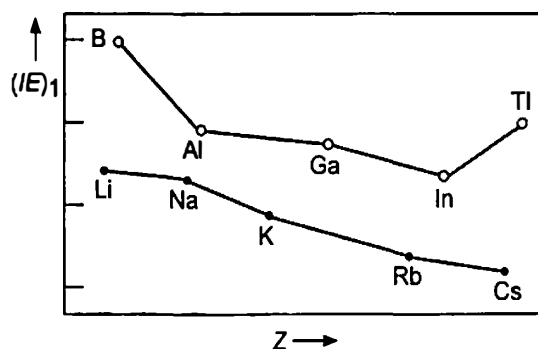


Fig. 3.6 Variation of  $(IE)_1$  of groups 1 (●) and 13 (○), (not according to scale)

### DEEP Focus

In general the first ionisation energy decreases in a regular way on descending the main groups. A departure from this trend occurs in group 13 (boron family), where the expected decrease occurs between B and Al, but the values for the remaining elements Ga, In and Tl do not continue the trend and are irregular. Ga with completely filled  $3d$ -orbitals (no  $3d$  in Al) decreases screening thus Ga is smaller in size than it would otherwise be.

|    | $(IE)_1$ in $\text{kJ mol}^{-1}$ |    | $(IE)_1$ |          |
|----|----------------------------------|----|----------|----------|
|    | Group 1                          |    | Group 13 |          |
| Li | 520                              | B  | 801      |          |
| Na | 496                              | Al | 577      | decrease |
| K  | 419                              | Ga | 579      | constant |
| Rb | 403                              | In | 558      | decrease |
| Cs | 376                              | Tl | 589      | increase |
|    | decrease                         |    |          |          |

As expected the first ionisation energies decrease down the groups in case of the main group elements in the Periodic Table. But in case of transition elements opposite trends are observed. Thus,  $(IE)_1$  of the corresponding elements of  $3d$  and  $4d$ -series are almost similar but these are smaller than the  $(IE)_1$  of the  $5d$ -series elements. Certainly, the higher values of ionisation energies of the  $5d$ -transition elements are consistent with the relatively small size of the atoms.

## Variation of $(IE)$ in a Period

On moving across a period, the atomic size decreases and nuclear charge increases and therefore the force of attraction exerted by the nucleus on the electron in outer most shell increases. Hence  $(IE)$  **increases along a period** from left to right. Fig. 3.7 explains general variation of  $(IE)$  in a group and period. Fig. 3.8 shows the pattern of the ionisation energies of the elements H to Ca.

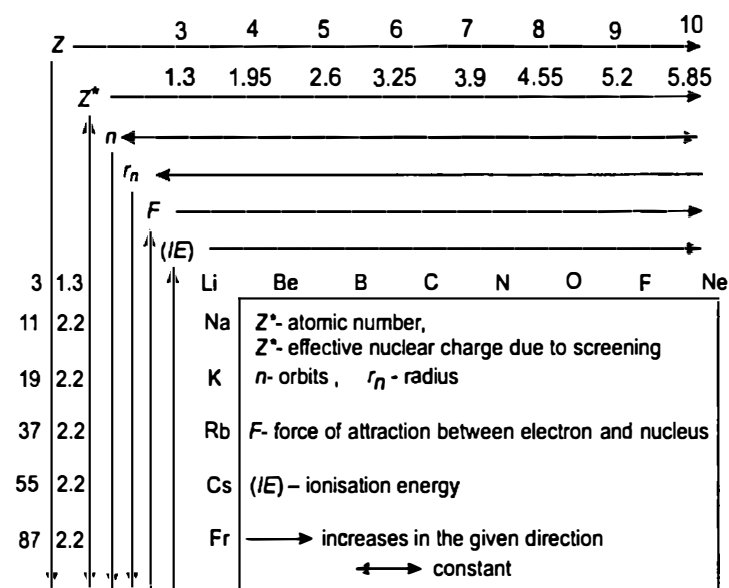


Fig. 3.7 Variation of  $(IE)$  in a group and period

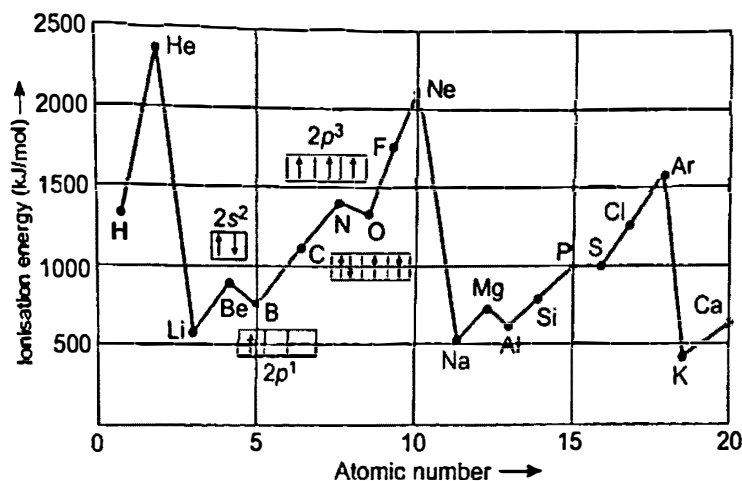


Fig. 3.8 Variation of IE with atomic number showing apparent anomalies of B and O, and Al and S

### DEEP Focus

- There are two bumps, or dips, around beryllium / boron and nitrogen / oxygen. The dip from beryllium to boron occurs because the extra electron of boron enters a  $2p$ -orbital, and this electron will feel the effects of the shielding by the pair of electrons in  $2s$ -orbital. The shielding has the effect of lowering of (IE). The increase from boron to carbon reflects the increased nuclear charge of carbon. Also, because the two  $2p$ -electrons of carbon are in different orbitals, they have little shielding effect on one another. A similar state of affairs accounts for the rise from carbon to nitrogen.
- The dip from nitrogen to oxygen is a different matter. Compared to nitrogen, the oxygen atom's extra electron must go into a  $2p$ -orbital that already has one electron in it. Putting two electrons into the same orbital brings about repulsion between them. For this reason it is easier to remove an electron from the  $2p$ -orbital in oxygen containing two electrons than it is from a similar orbital in nitrogen containing only one electron. This effect overweighs the effect of nuclear charge from nitrogen to oxygen.
- From oxygen to neon, the increase in ionisation energy reflects the increase in nuclear charge. In a general trend, there will be peaks for noble gases for the values of (IE).
- As Fig. 3.8 shows, metals have relatively low IE compared to non-metals.
- The IE, of the metalloids generally fall between those of metals and non-metals. The difference in IE suggests why metals always form cations and non-metals form anions.
- It is relatively easy to remove an electron from a partially filled valence shell, where  $Z_{\text{eff}}$  is lower but it is relatively difficult to remove an electron from an atom or ion that has a filled valence shell, when  $Z_{\text{eff}}$  is higher. In other words, there is a large amount of stability associated with filled  $s$  and  $p$ -subshells (a noble gas electron configuration), which corresponds to having eight electrons (an octet) in the valence shell of an atom or ion. Thus,

- sodium ( $[\text{Ne}] 3s^1$ ) loses one electron easily
- magnesium ( $[\text{Ne}] 3s^2$ ) loses only two electrons easily,
- aluminium ( $[\text{Ne}] 3s^2 3p^1$ ) loses only three electrons easily, and so on.

8 electron in valence shells

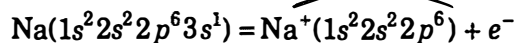


**Illustration 1** Two atoms have the electronic configurations (EC)  $1s^2 2s^2 2p^6$  and  $1s^2, 2s^2 2p^6 3s^1$ . (IE)<sub>1</sub> of one is  $2080 \text{ kJ mol}^{-1}$  and that of the other is  $496 \text{ kJ mol}^{-1}$ . Match each (IE)<sub>1</sub> with one of the given (EC). Justify your choice.

### Solution

| Element | (EC)                  |                                                                                                                                                                                                                                                                                                                                             |
|---------|-----------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| A       | $1s^2 2s^2 2p^6$      | $\begin{array}{ c } \hline \uparrow\downarrow \\ \hline 1s^2 \end{array}$ $\begin{array}{ c } \hline \uparrow\downarrow \\ \hline 2s^2 \end{array}$ $\begin{array}{ c c c } \hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow \\ \hline 2p^6 \end{array}$                                                                 |
|         |                       | stable inert gas EC and removal of electron requires higher energy                                                                                                                                                                                                                                                                          |
| B       | $1s^2 2s^2 2p^6 3s^1$ | $\begin{array}{ c } \hline \uparrow\downarrow \\ \hline 1s^2 \end{array}$ $\begin{array}{ c } \hline \uparrow\downarrow \\ \hline 2s^2 \end{array}$ $\begin{array}{ c c c } \hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow \\ \hline 2p^6 \end{array}$ $\begin{array}{ c } \hline \uparrow \\ \hline 3s^1 \end{array}$ |
|         |                       | has unpaired electron, removal of electron requires lower energy                                                                                                                                                                                                                                                                            |

Thus (IE)<sub>1</sub> of A is  $2080 \text{ kJ mol}^{-1}$  and that of B is  $496 \text{ kJ mol}^{-1}$ .

**Illustration 2** Arrange the elements Se, Cl and Si in increasing order of ionisation energy.

**Solution** Ionisation energy generally increases from left to right across a row of the Periodic Table and decreases from top to bottom down a group.

(IE) increases  
 $\begin{array}{c} \text{Si}_{14} \text{---} \text{Cl}_{17} \\ \uparrow \\ \text{Se}_{34} \end{array}$   
 decreases  
 Thus, (IE) of Cl > Si  
 and (IE) of Se < Si  
 Thus, the order is : Se < Si < Cl.

**Illustration 3** Which has the larger fifth ionisation energy, Ge or As?

### Solution

|                                           | Group    |
|-------------------------------------------|----------|
| Ge (32) : $[\text{Ar}] 4s^2 3d^{10} 4p^2$ | IVA (14) |
| As (33) : $[\text{Ar}] 4s^2 3d^{10} 4p^3$ | VA (15)  |

As their positions in the Periodic Table indicate, the group IVA (14) element Ge has four valence-shell electrons and thus four relatively low ionisation energies, whereas the group VA (15) element As has five valence-shell electrons and five low ionisation energies. Ge thus has larger fifth ionisation energy than As.

## Target Practice 2

1. Arrange the following atoms in order of increasing ionisation energy :

Si, K, P, Ca .....

2. Answer each of the following questions.

- (a) Of the elements S, Se and Cl which has the largest atomic radius? .....
- (b) Which has the layer radius, Br or Br<sup>-</sup> ? .....
- (c) Which should have the largest difference between the first and second ionisation energy : Si, Na, P or Mg? .....

- (d) Which has the largest ionisation energy? .....
- N, P, As

- (e) Which of the following has the largest radius? ...

O<sup>2-</sup>, N<sup>3-</sup> or F<sup>-</sup>

3. Select the atom or ion in each pair that has the radius

(a) Cl or Cl<sup>-</sup> .....

(b) Al or O .....

(c) I or I<sup>+</sup> .....

4. If screening effect is not considered, and thus effective nuclear charge is the atomic number, then

(a) larger radius out of Li, Be is .....

(b) larger ionisation potential out of Li, Na is .....

(c) larger radius out of Li, Na is .....

## Answers

1. K < Ca < Si < P

2. (a) Se (b) Br<sup>-</sup>

(c) Na (since Na<sup>+</sup> attains stable inert gas configuration)

(d) N (e) N<sup>3-</sup>

3. (a) Cl<sup>-</sup> (b) Al (c) I

4. (a)  $r_n = \frac{n^2 a_0}{2}$

$$r_n(\text{Li}) = \frac{490}{3}$$

$$r_n(\text{Be}) = \frac{490}{4}$$

Thus,

$$r_n(\text{Be}) < r_n(\text{Li})$$

Thus, Li

$$(b) \quad (IE)_Z = (IE)_H \frac{Z^2}{n^2}$$

$$(IE)_{\text{Li}} = (IE)_H \left( \frac{9}{4} \right) = (2.25) (IE)_H$$

$$(IE)_{\text{Na}} = (IE)_H \left( \frac{121}{9} \right) > (IE)_{\text{Li}}$$

Thus, Na

$$(c) \quad r_n(\text{Na}) = \frac{990}{11} < r_n(\text{Li})$$

(as in Cl (a))

Thus, Li

## Practice Exercise 2

1. There is recurrence of properties after 2, 8, 8, 18, 18 and 32 elements in the Periodic Table. Explain.

2. What would be the number of elements of recurrence of properties if each orbital can take three electrons instead of two?

3. Group the following electronic configurations in pairs that would represent similar chemical properties of their atoms :

(a) 1s<sup>2</sup>, 2s<sup>2</sup> 2p<sup>5</sup>

(b) 1s<sup>2</sup>, 2s<sup>1</sup>

(c) 1s<sup>2</sup>, 2s<sup>2</sup> 2p<sup>6</sup>

(d) 1s<sup>2</sup>, 2s<sup>2</sup> 2p<sup>6</sup>, 3s<sup>2</sup> 3p<sup>5</sup>

(e) 1s<sup>2</sup>, 2s<sup>2</sup> 2p<sup>6</sup>, 3s<sup>2</sup> 3p<sup>6</sup>, 4s<sup>1</sup>

(f) 1s<sup>2</sup>, 2s<sup>2</sup> 2p<sup>6</sup>, 3s<sup>2</sup> 3p<sup>6</sup>, 4s<sup>2</sup> 3d<sup>10</sup> 4p<sup>6</sup>

4. The boiling points of neon and krypton are -245.9°C and -152.9°C respectively. Using these data estimate the boiling point of argon.

5. Which of the following properties show a clear periodic variation along a group?

(a) First ionisation energy

(b) Molar mass of the elements

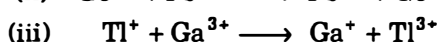
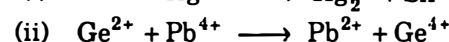
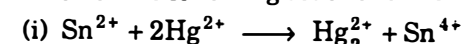
(c) Number of isotopes of an element

(d) Atomic radius.

6. Pb<sup>4+</sup> salts are better oxidising agents while Ge<sup>2+</sup> salts are better reducing agents. Explain.

7. BiCl<sub>5</sub> does not exist. Explain.

8. Which of the following reactions are not possible/po



9. Determine value of effective nuclear charge of

(i) Mg (Z = 12)

(ii) Sc (Z = 21)

(iii) Cu (Z = 29)

10. He and He<sup>+</sup> have different size though each has same of Z and same number of orbit (n = 1). Explain. You n

$$\text{equation } r_n = \frac{n^2 a_0}{Z}$$

11. Ionisation potential (IP) of the element/ion with number Z is given by

$$(IP)_Z = 13.6 \left( \frac{Z^2}{n^2} \right) \text{ eV.}$$

Compare values of IP of He and He<sup>+</sup>.

12. Ionisation potential of Be<sup>2+</sup> is found to be 217.6 eV v the first orbit. What is the value of x?

13. Compare atomic radii of third period elements moving left to right.

14. As we shall be taking in further chapters, covalent radii of Cr(24) to Cu(29) do not vary appreciably. Explain.

|             | Cr <sub>24</sub> | Mn <sub>25</sub> | Fe <sub>26</sub> | Co <sub>27</sub> | Ni <sub>28</sub> | Cu <sub>29</sub> |
|-------------|------------------|------------------|------------------|------------------|------------------|------------------|
| radius (pm) | 117              | 117              | 117              | 116              | 115              | 117              |

15. Referring to the Periodic Table, arrange the following atoms in order of increasing radius  
(a) P, Si, N (b) Na<sup>+</sup>, Cl<sup>-</sup>, O<sup>2-</sup>, Ne
16. On the basis of their positions in the Periodic Table, select the atom with the larger atomic radius in each of the following pairs :  
(a) Na, Cs (b) Be, Ba  
(c) N, Sb (d) F, Br  
(e) Ne, Xe
17. Calculate atomic radius of Li and Na atoms  
(i) without consideration of screening  
(ii) with consideration of screening.  
Which gives better result ?
18. What is effective nuclear charge on Li if its radius is 1.23 Å ?
19. Compare the ionic size of :  
(a) Fe<sup>2+</sup> and Fe<sup>3+</sup> (b) Cu<sup>+</sup> and Cu<sup>2+</sup>  
(c) H<sup>+</sup>, H<sup>-</sup> and H
20. Arrange the following in increasing atomic radius :  
(i) Cr<sub>24</sub>, Mn<sub>25</sub>, Fe<sub>26</sub> (ii) Ni<sub>28</sub>, Cu<sub>29</sub>, Zn<sub>30</sub>  
(iii) Ge<sub>32</sub>, As<sub>33</sub>, Se<sub>34</sub> (iv) Tl<sub>81</sub>, Zr<sub>40</sub>, Hf<sub>72</sub>
21. Arrange the following in increasing radius :  
(i) Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> (ii) K<sup>+</sup>, Ca<sup>2+</sup>, Ar  
(iii) Mg, Mg<sup>+</sup>, Mg<sup>2+</sup> (iv) O<sup>2-</sup>, N<sup>3-</sup>, F<sup>-</sup>  
(v) O, O<sup>-</sup>, O<sup>2-</sup>
22. Calculate ionic radius of Li<sup>2+</sup>, Be<sup>3+</sup> and He<sup>+</sup> each containing one electron in the ground state.
23. For each of the following pairs, indicate which one of the two species is larger?  
(a) N<sup>3-</sup> or F<sup>-</sup> (b) Mg<sup>2+</sup> or Ca<sup>2+</sup>  
(c) Fe<sup>2+</sup> or Fe<sup>3+</sup> (d) Na<sup>+</sup> or Ne  
(e) Au<sup>+</sup> or Au<sup>3+</sup> (f) P<sup>3-</sup> or N<sup>3-</sup>
24. The atomic radius of F is 72 pm and that of F<sup>-</sup> is 136 pm. Calculate the per cent increase in volume that occurs when F(g) is converted to F<sup>-</sup>(g).
25. IE (in kJ mol<sup>-1</sup>) of Li and Be are given below :

|    | Z | (IE) <sub>1</sub> | (IE) <sub>2</sub> | (IE) <sub>3</sub> |
|----|---|-------------------|-------------------|-------------------|
| Li | 3 | 520.1             | 7297              | 11810             |
| Be | 4 | 899.3             | 1758              | 14810             |

(IE)<sub>2</sub> of Li is much higher than that of its (IE)<sub>1</sub> but in case of Be (IE)<sub>3</sub> is much higher than that of its (IE)<sub>1</sub>. Explain.

26. Can you identify the element of third period whose successive (IEs) are given below :

| Element | (IE) <sub>1</sub> | (IE) <sub>2</sub> | (IE) <sub>3</sub> |
|---------|-------------------|-------------------|-------------------|
| X       | 513               | 4562              | 6920              |
| Y       | 738               | 1451              | 7733              |
| Z       | 1521              | 2666              | 3931              |

27. (IE) of Na is 513 kJ mol<sup>-1</sup>. What is value in eV molecule<sup>-1</sup>?

28. Which element in each of the following pairs has the larger ionisation energy (IE)?  
(a) K or Br (b) S or Te  
(c) Ga or Se (d) Ne or Sr

29. For one-electron species, (IE) is given by

$$(IE) = 13.6 \left( \frac{Z^2}{n^2} \right) \text{eV}$$

Calculate (IE) of He<sup>+</sup>, Li<sup>2+</sup> and Be<sup>3+</sup>.

30. (IE)<sub>1</sub> < (IE)<sub>2</sub> for any case. Can you compare (IE) of He and He<sup>+</sup> using equation in Q. 29 above ?
31. (IE)<sub>1</sub> of Cs is 376 kJ mol<sup>-1</sup>. What is the maximum number of Cs<sup>+</sup> ions that can be produced per joule of energy absorbed by a sample of gaseous Cs atoms ?
32. Which atom should have a smaller value of (IE)<sub>1</sub>?  
(a) Oxygen or sulphur (b) Nitrogen or phosphorus
33. Which of the following atoms should have a smaller value of second (IE) : Na or Mg?
34. (a) Which has the larger third ionisation energy, Be or N?  
(b) Which has the larger fourth ionisation energy, Ga or Ge?
35. Three atoms have the following electron configurations:  
(i) 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>1</sup> (ii) 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>5</sup>  
(iii) 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>1</sup>  
(a) Which of the three has the largest (IE)<sub>1</sub> ?  
(b) Which has the largest (IE)<sub>4</sub> ?
36. Which has larger (IE) in each pair?  
(a) N or O<sup>+</sup> (b) Be<sup>+</sup> or B<sup>+</sup>  
(c) Be or B (d) Na<sup>+</sup> or Ne
37. (IE)<sub>1</sub> of Be is greater than that of (B) but (IE)<sub>2</sub> of (B) is greater than that of Be. Explain.
38. Match the electronic configuration with the values of (IE) of the elements in the *n*th period (*n* ≠ 1) :

|    | EC                              | (IE) kJ mol <sup>-1</sup> |
|----|---------------------------------|---------------------------|
| 1. | ns <sup>2</sup>                 | I 4000                    |
| 2. | ns <sup>2</sup> np <sup>1</sup> | II 1500                   |
| 3. | ns <sup>2</sup> np <sup>3</sup> | III 1200                  |
| 4. | ns <sup>2</sup> np <sup>6</sup> | IV 1400                   |

39. In general, ionisation energy increases from left to right across a given period. Aluminium, however, has a lower ionisation energy than magnesium. Explain.
40. (IE)<sub>1</sub> and (IE)<sub>2</sub> in kJ mol<sup>-1</sup> of K and Ca have been given as

|    | (IE) <sub>1</sub> | (IE) <sub>2</sub> |
|----|-------------------|-------------------|
| K  | 419               | 3052              |
| Ca | 590               | 1145              |

Compare their values and comment on the differences.

41. Arrange the following isoelectronic species in order of  
(a) increasing ionic radius and  
(b) increasing (IE)  
O<sup>2-</sup>, F<sup>-</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>
42. The first four ionisation energies of an element (in kJ mol<sup>-1</sup>) are approximately 738, 1450, 7.7 × 10<sup>3</sup> and 1.1 × 10<sup>4</sup>. To which periodic group does this element belong? Why?
43. Which element in each of the following sets has the smallest first ionisation energy, and which has the largest?  
(a) Li, Ba, K (b) B, Be, Cl  
(c) Ca, C, Cl





21. (i)  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$  (ii)  $\text{Ca}^{2+} < \text{K}^+ < \text{Ar}$   
 (iii)  $\text{Mg}^{2+} < \text{Mg}^+ < \text{Mg}$  (iv)  $\text{F}^- < \text{O}^{2-} < \text{N}^{3-}$   
 (v)  $\text{O} < \text{O}^- < \text{O}^{2-}$

22. Radius of  $\text{Li}^{2+} = 0.1763 \text{ \AA}$

$$\left. \begin{array}{l} \text{Be}^{3+} = 0.1323 \text{ \AA} \\ \text{He}^+ = 0.2645 \text{ \AA} \end{array} \right\} \text{use equation } r_n = \frac{n^2 a_0}{Z}$$

In this case,  $Z = Z^*$  since each contains one electron and no screening takes place, i.e.,  $\sigma = 0$ .

23. (a)  $\text{N}^{3-}$  (b)  $\text{Ca}^{2+}$  (c)  $\text{Fe}^{2+}$  (d)  $\text{Ne}$  (e)  $\text{Au}^+$  (f)  $\text{P}^{3-}$

24.  $5.74 \times 10^2 \%$

25.  $(IE)_2$  of Li involves removal of electron from  $\text{Li}^+ (1s^2)$  which has inert gas (stable) helium configuration, hence  $(IE)_2$  of Li  $\gg \gg (IE)_1$ .  $(IE)_3$  of Be involves removal of electron from  $\text{Be}^{2+} (1s^2)$  which is again stable hence  $(IE)_3$  of Be  $\gg \gg (IE)_1$

26. X: Na its  $(IE)_2$  is very high

Y: Mg its  $(IE)_3$  is very high

Z: Ar its  $(IE)_1$  is very high

27.  $513 \text{ kJ mol}^{-1} = \frac{513000 \text{ J}}{6.02 \times 10^{23}} \text{ molecule}^{-1}$   
 $= 8.522 \times 10^{-19} \text{ J molecule}^{-1}$   
 $= \frac{8.522 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV} = 5.326 \text{ eV}$

28. (a) Br (b) S (c) Se (d) Ne

| Species          | (IE)     |                                                                         |
|------------------|----------|-------------------------------------------------------------------------|
| $\text{He}^+$    | 54.4 eV  | Being single electron species, $Z^* = Z$ (there is no screening effect) |
| $\text{Li}^{2+}$ | 122.4 eV |                                                                         |
| $\text{Be}^{3+}$ | 217.6 eV |                                                                         |

30. In case of He, there is screening by one electron hence  $Z^* = 1.7$

$$(IE)_{\text{He}} = 13.6 \times (1.7)^2 = 39.4 \text{ eV},$$

$$(IE)_{\text{He}^+} = 54.4 \text{ eV (in Q. 29)}$$

31.  $376 \text{ kJ mol}^{-1}$

$$376 \times 10^3 \text{ J mol}^{-1}$$

$$376 \times 10^3 \text{ J ionise} = 1 \text{ mol}$$

$$= 6.02 \times 10^{23} \text{ atoms}$$

$$1 \text{ J ionises} = \frac{6.02 \times 10^{23}}{376 \times 10^3} \text{ atoms}$$

$$= 1.6 \times 10^{18} \text{ atoms}$$

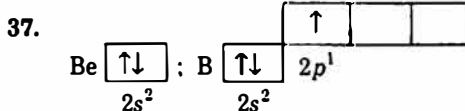
32. (a) S (b) P 33. Mg

34. (a) Be (b) Ga

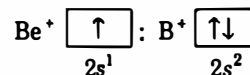
35. (a) largest  $(IE)_1 = (\text{ii})$

- (b) largest  $(IE)_4 = (\text{i})$

36. (a)  $\text{O}^+$  (b)  $\text{B}^+$  (c) Be (d)  $\text{Na}^+$



Unpaired electron in B is easier to remove than that paired electron in Be. Hence  $(IE)_1$  of Be  $>$   $(IE)_1$  of B, and by  $(IE)_1$   $\text{Be}^+$  and  $\text{B}^+$  are formed.



Now reverse is the case; removal of unpaired electron from  $\text{Be}^+$  is easier than that of paired electron from  $\text{B}^+$ . Hence  $(IE)_2$  of B  $>$   $(IE)_2$  of Be.

|   | EC | (IE) |
|---|----|------|
| 1 |    | III  |
| 2 |    | IV   |
| 3 |    | II   |
| 4 |    | I    |

39. Refer Text

40.  $(IE)_2$  of K  $\gg \gg (IE)_1$  of K since  $\text{K}^+$  (after one electron is removed) has stable inert gas configuration as compared to corresponding values for Ca in which  $\text{Ca}^+$  can lose second electron easily.

41. (a)  $\text{Mg}^{2+} < \text{Na}^+ < \text{F}^- < \text{O}^{2-}$  (b)  $\text{O}^{2-} < \text{F}^- < \text{Na}^+ < \text{Mg}^{2+}$

42. Alkaline earth elements.

- 43.

|     | Min | Max |
|-----|-----|-----|
| (a) | K   | Li  |
| (b) | B   | Cl  |
| (c) | Ca  | Cl  |

44. (a) II (b) IV (c) I (d) III

## Electron Affinity (EA)

Electron affinity (EA) is the amount of energy associated with the gain of electrons by the gaseous atom.



Electron affinity is also called **electron gain enthalpy**. The sign of the enthalpy change indicates that this is an exothermic process; however the electron affinity of fluorine is assigned a value of  $+328 \text{ kJ mol}^{-1}$ . Thus, we can think of electron affinity as the energy that must be supplied to remove an electron from a negative ion.

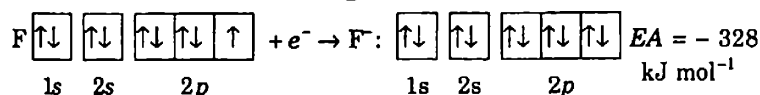


## DEEP Focus

Two features of electron affinity based on above line to remember are :

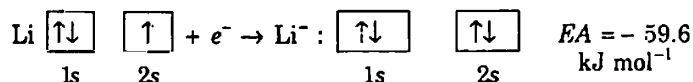
- (1) The electron affinity of an element is equal to the enthalpy change that accompanies the ionisation process of its ion.
  - (2) A large positive electron affinity means that the negative ion is very stable (that is, the atom has greater tendency to accept an electron).
- The greater the energy released in the process of taking up the extra electron, the greater is the electron affinity.
  - The electron affinity of an atom measures the tightness with which it binds an additional electron to itself.

- In terms of orbital diagram:

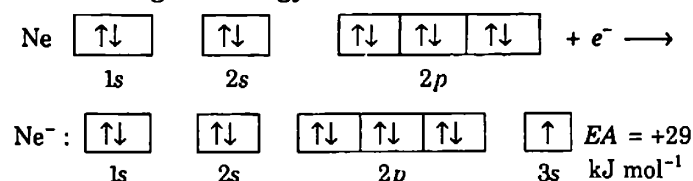


In becoming  $\text{F}^-$ , fluorine acquires the electron configuration of noble gas (Ne).

- By the line of reasoning outlined above, we might expect that even metal atoms can form negative ions in the gaseous state, and this happens too.



- There are also cases when addition of electron experience repulsion; in such cases ( $EA$ ) is a positive quantity. This is the case for the noble gases [group 18 (VIII A)], where the added electron goes into  $(n+1)s$  orbital of higher energy.



- The group 2 (IIA) elements with filled  $s$ -subshell ( $ns^2$ ), also have positive ( $EA$ ).
- Even better examples of positive electron affinities are those associated with gaining a second electron. Here the electron to be added is approaching not a neutral atom but a negative ion. A strong repulsion is felt and the energy of the system increases.



This process  $[\text{O}^-(g) + e^- \longrightarrow \text{O}^{2-}(g)]$  is unfavourable in the gas phase because the resulting increase in electron-electron repulsion outweighs the stability gained by achieving the noble gas configuration. However, note that  $\text{O}^{2-}$  is common in ionic compounds; in solids,  $\text{O}^{2-}$  is stabilised by neighbouring cations.

- ( $EA$ ) values ( $\text{kJ mol}^{-1}$ ) of some elements are given below :

|   |             |             |  |            |             |            |            |              |              |            |
|---|-------------|-------------|--|------------|-------------|------------|------------|--------------|--------------|------------|
| 1 | H<br>-72    |             |  |            |             |            |            |              | He<br>(21)   |            |
| 2 | Li<br>-60   | Be<br>(241) |  | B<br>-23   | C<br>-122   | N<br>0     | O<br>-142  | F<br>-328    | Ne<br>(29)   |            |
| 3 | Na<br>-53   | Mg<br>(231) |  | Cu<br>-123 | Al<br>-44   | Si<br>-119 | P<br>-74   | S<br>-200    | Cl<br>-348   | Ar<br>(35) |
| 4 | K<br>-48    | Ca<br>(156) |  | Ag<br>-125 | Ga<br>(-36) | Ge<br>-116 | As<br>-77  | Se<br>-194   | Br<br>-323   | Kr<br>(39) |
| 5 | Rb<br>-47   | Sr<br>(119) |  | Au<br>-222 | In<br>(-34) | Sn<br>-120 | Sb<br>-101 | Te<br>-190   | I<br>-295    | Xe<br>(40) |
| 6 | Cs<br>-45   | Ba<br>(52)  |  |            | Tl<br>(-48) | Pb<br>-101 | Bi<br>-101 | Po<br>(-173) | At<br>(-270) | Rn<br>(40) |
| 7 | Fr<br>(-44) |             |  |            |             |            |            |              |              |            |

\*Estimated value are in parentheses

## Variation of ( $EA$ ) in a Period

- On moving across a period, the atomic size decreases and hence, the force of attraction exerted by the nucleus on the electrons increases. Consequently, the atom has a greater tendency to attract additional electron, i.e., its electron affinity increases.
- Also ( $EA$ ) values of metals are low while those of non-metals are high.
- Halogens have high electron affinities. This is due to their strong tendency to gain an additional electron to change into the stable  $ns^2np^6$  configuration.

## Variation of ( $EA$ ) in a Group

On moving down a group, the atomic size increases and, therefore, the effective nuclear attraction decreases and thus, electron affinity decreases.

### DEEP Focus

- The fact that fluorine has a less negative electron affinity than chlorine seems to be due to the relatively greater effectiveness of  $2p$ -electrons in the small F atom to repel the additional electron entering the atom than do the  $3p$ -electrons in the larger Cl atom.
- The results have been represented in Fig. 3.9.

The positive value of ( $EA$ ) of Be, Mg and N are also interesting. The stability of the filled  $s$ -shell (in Be and Mg) and half-filled  $p$ -shell (in N) and the resulting reluctance of these atoms to add any extra electron is indicated.

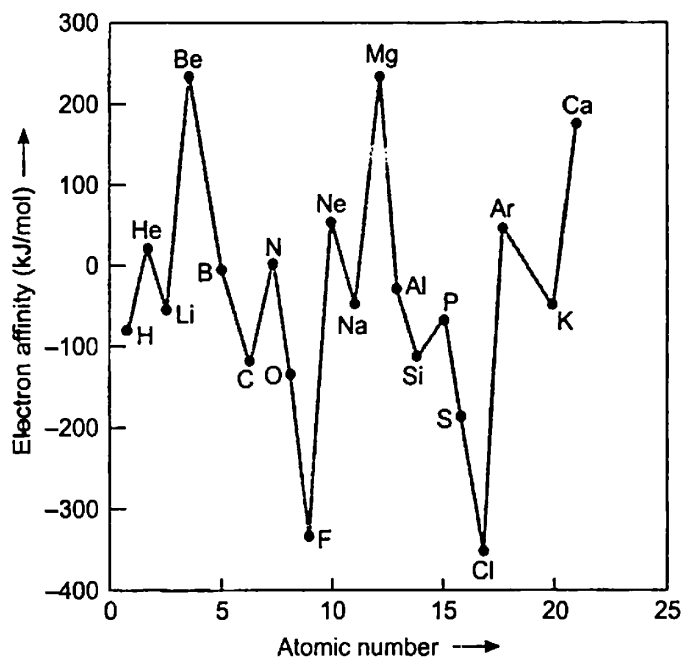
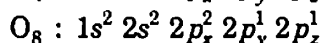
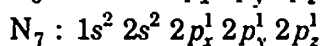
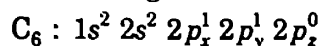


Fig. 3.9 A plot of electron affinity versus atomic number for the first 20 elements. The general horizontal trend is that electron affinities become more negative (more energy is released as an extra electron is added) from group IA (1) through group VIIA (17) for a given period. Exceptions occur at the IIA (2) and VA (15) elements.

**Illustration 1** Why does nitrogen have a less favourable (more positive) electron-affinity than its neighbours on either side, C and O?

**Solution** Electron configurations of these elements are :



Carbon has only two electrons in its  $2p$ -subshell and can readily accept another in its vacant  $2p_z$ -orbital. Nitrogen, however, has a half-filled  $2p$ -subshell, and the additional electron must pair up in a  $2p$ -orbital, when it feels a repulsion from the electron already present.

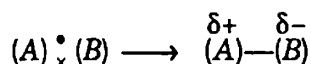
Thus the electron affinity of nitrogen is less favourable than that of carbon. Oxygen also must add an electron to an orbital that already has one electron, but the additional stabilising effect of increased effective nuclear charge ( $Z_{\text{eff}}$ ), across the Periodic Table counteracts the effect of electron repulsion, resulting in a more favourable electron-affinity for O than for N.

## Electronegativity (EN)

Electronegativity is a measure of the tendency of an element to attract electrons to itself.



In a molecule, tendency of the atom to attract bonding pair towards itself is its electronegativity. B is said to be more electronegative than A if it pulls bonding pair towards itself.



The absolute magnitude of the electronegativity value (EN) of an element is however not fixed. Different values may be assigned to the same element from different theoretical approaches. Accordingly, different (EN) scales have been suggested.

## Variation of (EN) in a Group

- On moving down the group
- $Z$  increases but  $Z^*$  almost remains constant,
- number of shells ( $n$ ) increases,
- $r_n$  (atomic radius) increases,
- force of attraction  $\left(F = \frac{kZe^2}{r_n^2}\right)$  between added electron and nucleus decreases,

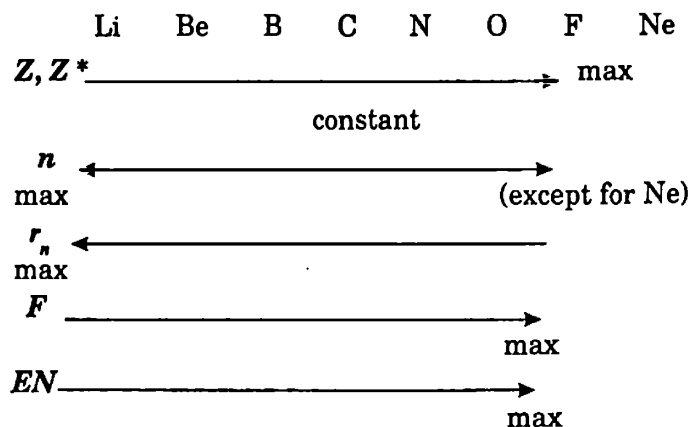
Therefore, (EN) decreases moving down the group.

| Element | Z  | $Z^*$    | $n$ | $r_n$ | F     | (EN)  |
|---------|----|----------|-----|-------|-------|-------|
| F       | 9  | ↑        | ↓   | ↓     | ↑ max | ↑ max |
| Cl      | 17 | ↑        | ↓   | ↓     | ↑ max | ↑ max |
| Br      | 35 | ↑        | ↓   | ↓     | ↑ max | ↑ max |
| I       | 53 | ↑        | ↓   | ↓     | ↑ max | ↑ max |
|         |    | constant | max | max   |       |       |

## Variation of (EN) in a Period

- While moving across a period left to right
- $Z, Z^*$  increases,
- $n$  (number of shells) remains constant,
- $r_n$  decreases,
- $F \left( = k \frac{Ze^2}{r_n^2} \right)$  increases

hence, (EN) increases along a period.



- Fluorine is the most electronegative element in the Periodic Table.

Fig. 3.10 represents variation of electronegativity of elements with atomic number. In this :

- the strongest non-metals, the halogens, appear at the peaks;

the alkali metals mark the troughs. This is largely a result of new shell of electrons starting with noble gases which have zero values of electronegativities.

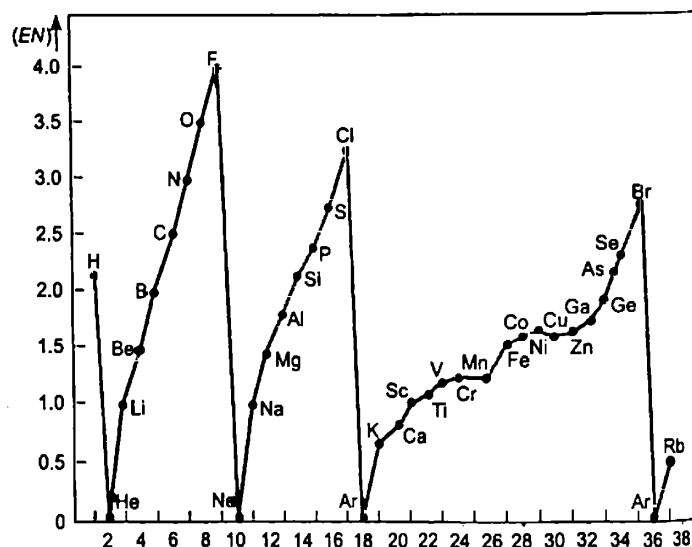
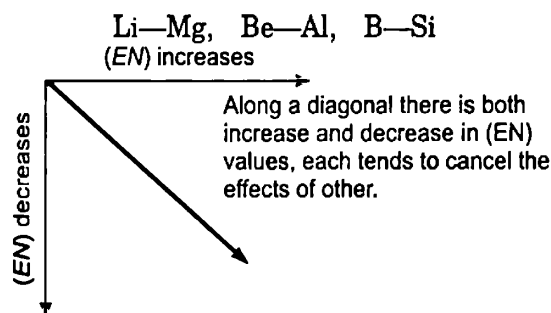


Fig. 3.10 Electronegativities of the elements H(1) to Rb (37). The (EN) of the noble gases have been set at zero.

- the group 1 (IA) metals have their nuclei quite strongly shielded. Hence, they show little tendency to gain new electron.
- the electronegativities of transition metals like their (IE), do not change greatly from one another.

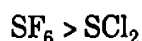
## Diagonal Relationship and Electronegativity

- Moving one place to the right across period, the increased nuclear charge holds the electrons more tightly to the atom. Moving down one place in a group, the extra shell of electrons decreases the attraction of the nucleus for the outer electrons. A **diagonal** move means that these effects tend to compensate for one another.
- The electronegativity increases as we go from Li to Be but it decreases as we move from Be to Mg. As we move diagonally, these two effects partly cancel each other and there is no marked change in electronegativity and thus Li and Mg have close values of electronegativities. Because of this, Li and Mg show similarity in properties— a diagonal relationship (between elements lying diagonally in Periodic Table).
- Elements' pairs showing this relationship are :



### DEEP Focus

Electronegativity of an element depends on its valence state and hence it will change from one compound or one bonding situation to another. An atom will have a greater attraction for electrons when its oxidation state is high, rather than when it is in a low oxidation state — increase of positive oxidation state or formal charge of an atom increases its (EN). Thus, (EN) value of sulphur in



|          |      |
|----------|------|
| Fe (II)  | 1.83 |
| Fe (III) | 1.96 |
| Tl (I)   | 1.62 |
| Tl (III) | 2.04 |
| Sn (II)  | 1.80 |
| Sn (IV)  | 1.96 |
| Pb (II)  | 1.87 |
| Pb (IV)  | 2.33 |

### DEEP Focus

Hybrid orbitals with greater *s*-character should be more electronegative than hybrid orbitals with less *s*-character. As *s*-character increases, (EN) value increases hence acidic character increases.

|                         |               |                        |                        |
|-------------------------|---------------|------------------------|------------------------|
|                         | $\text{CH}_4$ | $\text{C}_2\text{H}_4$ | $\text{C}_2\text{H}_2$ |
| hybridization of C-atom | $sp^3$        | $sp^2$                 | $sp$                   |
| <i>s</i> -character     | 25%           | 33.3%                  | 50%                    |
| (EN)                    | →             |                        |                        |
| acidic nature           | →             |                        |                        |

The estimated values (in Pauling equivalents) for C and N in different hybridization states are :

| Atom | $sp^3$ | $sp^2$ | $sp$ |
|------|--------|--------|------|
| C    | 2.5    | 2.75   | 3.3  |
| N    | 3.7    | 3.9    | 4.7  |

Thus, carbon in  $\text{C}_2\text{H}_2$  is more electronegative than chlorine; *sp*-hybridised nitrogen is more electronegative than fluorine.

## Pauling's Electronegativity

Let us consider two covalent molecules  $\text{H—H}$  and  $\text{X—X}$



The above reaction is generally exothermic, the bond  $\text{H—X}$  is thus more stable and hence stronger than either of the bonds  $\text{H—H}$  or  $\text{X—X}$ . If the bond  $\text{H—X}$  were purely covalent (like the bonds  $\text{H—H}$  or  $\text{X—X}$ , i.e., the electron pair forming the bond would have been equally shared by H and X, the bond  $\text{H—X}$  would not be so. Pauling suggested that extra stability was derived from unequal sharing of the bonding electrons between A and B, giving rise to some ionic character. The extent of this ionic character, as measured by the extra stability of the bond, is dependent on unequal sharing of the bonding electrons, which depends on the (EN) difference of H and X. Extra stability of the bond  $\text{H—X}$  has been correlated to the difference in (EN).

This scale determines electronegativity of the element X w.r.t. hydrogen H

$$\chi_X - \chi_H = 0.208 \sqrt{\Delta_{\text{H-X}}}$$

where  $\chi$  (chi) represents electronegativity,  $\Delta_{\text{H-X}}$  is the extra bond energy in  $\text{kcal mol}^{-1}$

$$\text{and } \Delta_{\text{H-X}} = E_{\text{H-X}} - \sqrt{E_{\text{H-H}} E_{\text{X-X}}}$$

$E_{\text{H-X}}$ ,  $E_{\text{H-H}}$  and  $E_{\text{X-X}}$  represent bond energy of  $\text{H—X}$ ,  $\text{H—H}$  and  $\text{X—X}$  bonds respectively.

Converting the equation to SI units

$$\chi_X - \chi_H = 0.1017 \sqrt{\Delta_{\text{H-X}}}$$

where  $\Delta_{\text{H-X}}$  is measured in  $\text{kJ mol}^{-1}$ .

- $\chi_H = 2.05$  (and not zero) to avoid any negative value of the element.

Some other elements have following values of electronegativity based on Pauling's scale :

|                 |                 |                 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |               |
|-----------------|-----------------|-----------------|--|--|--|--|--|--|--|--|--|--|--|--|--|--|---------------|
| (1)<br>IA       |                 |                 |  |  |  |  |  |  |  |  |  |  |  |  |  |  | (18)<br>VIIIA |
| 1<br>H<br>2.1   | (2)<br>IIA      |                 |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 2<br>He       |
| 3<br>Li<br>1.0  | 4<br>Be<br>1.5  |                 |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 10<br>Ne      |
| 11<br>Na<br>1.0 | 12<br>Mg<br>1.2 | (3)<br>IIIB     |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 18<br>Ar      |
| 19<br>K<br>0.9  | 20<br>Ca<br>1.0 | 21<br>Sc<br>1.3 |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 36<br>Kr      |
| 37<br>Rb<br>0.9 | 38<br>Sr<br>1.0 | 39<br>Y<br>1.2  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 54<br>Xe      |
| 55<br>Cs<br>0.8 | 56<br>Ba<br>1.0 | 57<br>La<br>1.1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 86<br>Rn      |
| 87<br>Fr<br>0.8 | 88<br>Ra<br>1.0 | 89<br>Ac<br>1.1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |               |

|                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 58<br>Ce<br>1.1 | 59<br>Pr<br>1.1 | 60<br>Nd<br>1.1 | 61<br>Pm<br>1.1 | 62<br>Sm<br>1.1 | 63<br>Eu<br>1.1 | 64<br>Gd<br>1.1 | 65<br>Tb<br>1.1 | 66<br>Dy<br>1.1 | 67<br>Ho<br>1.1 | 68<br>Er<br>1.1 | 69<br>Tm<br>1.1 | 70<br>Yb<br>1.0 | 71<br>Lu<br>1.2 |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|

|                 |                 |                |                 |                 |                 |                 |                 |                 |                 |                  |                  |                  |                  |
|-----------------|-----------------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|------------------|------------------|------------------|------------------|
| 90<br>Th<br>1.2 | 91<br>Pa<br>1.3 | 92<br>U<br>1.5 | 93<br>Np<br>1.3 | 94<br>Pu<br>1.3 | 95<br>Am<br>1.3 | 96<br>Cm<br>1.3 | 97<br>Bk<br>1.3 | 98<br>Cf<br>1.3 | 99<br>Es<br>1.3 | 100<br>Fm<br>1.3 | 101<br>Md<br>1.3 | 102<br>No<br>1.3 | 103<br>Lr<br>1.5 |
|-----------------|-----------------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|------------------|------------------|------------------|------------------|

Electronegativity values are given at the bottoms of the boxes.

The noble gases are not included in this discussion.

- If two atoms have similar electronegativity, the bond between H and X will be predominantly covalent.
- A large difference in electronegativity leads to a bond with a high degree of polar character, and bond will be predominantly ionic.
- Ionic character of a bond varies with the difference in electronegativity as given in Fig. 8.11. This is based on the ionic character; HI : 4%, HBr : 11%, HCl : 19% and HF : 45% which are known from dipole moment measurements.

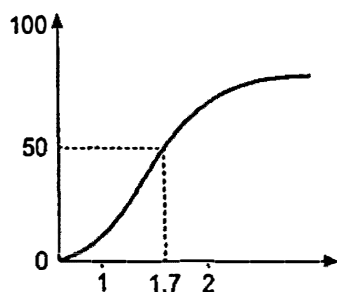


Fig. 3.11 Electronegativity difference

- 50% ionic character is shown in the cases when electronegativity difference is about 1.7.  
Thus,

$$\begin{aligned}
 (\chi_X - \chi_H) &= 1.7 && \text{50\% ionic} \\
 (\chi_X - \chi_H) &> 1.7 && \text{predominantly ionic} \\
 (\chi_X - \chi_H) &< 1.7 && \text{predominantly covalent}
 \end{aligned}$$

## Mulliken-Jaffe Electronegativity

Electronegativity ( $EN$ ) can be regarded as the average of the ionisation energy ( $IE$ ) and the electron affinity ( $EA$ ) of an atom.

$$(EN) = \frac{IE + EA}{2}$$

If both ( $EA$ ) and ( $IE$ ) are determined in eV units then Pauling's electronegativity ( $EN$ )<sub>P</sub> is related to Mulliken's electronegativity ( $EN$ )<sub>M</sub> by the equation :

$$(EN)_P = 0.336[(EN)_M - 0.615]$$

- If ( $EA$ ) and ( $IE$ ) are in eV, then ( $EN$ ) in eV is given by  

$$0.187(IE + EA) + 0.17$$
- Mulliken's values were about 2.8 times larger than the Pauling's values.

## Allred-Rochow's Electronegativity

Allred and Rochow defined electronegativity as the force exerted by the nucleus of an atom on its valence electrons :

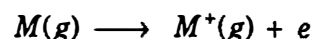
$$(EN)_{A-R} = \frac{0.359 Z_{\text{effective}}}{r^2} + 0.744$$

where  $Z_{\text{effective}}$  is the effective nuclear charge and  $r$  the covalent radius (in Å).

The relative ( $EN$ ) values of different elements in the same scale is extremely helpful in studying and predicting the nature of bonds formed between them.

## Metallic Nature

Metals have the tendency to form cations by loss of electrons and this property makes the elements as **electropositive** elements or metals.



- The tendency of an element to lose electron is closely connected to the ( $IE$ ) of the element. **The smaller the ( $IE$ ) of an element, the greater will be its tendency to lose electrons and thus greater will be its metallic character.**
- Tendency to oxidise itself provides reducing property to the elements thus, smaller the ( $IE$ ), greater the metallic character, hence greater the reducing nature : ( $IE$ ) increases moving along a period left to right and decreases down the group, hence metallic and reducing nature decrease along the period and increase down the group.

| Nuclear charge | Shielding | Tendency to make +ve ions                      | Reducing power | Metallic nature |
|----------------|-----------|------------------------------------------------|----------------|-----------------|
| increases      | increases | But the shielding effect wins so $\Rightarrow$ | increases      | increases       |

Notice that the most reactive metals (the top of the activity series) are on the left of the Periodic Table, whereas the least reactive metals (the bottom of the activity series) are in the transition metal groups closer to the right side of the table as shown in Fig. 3.12.

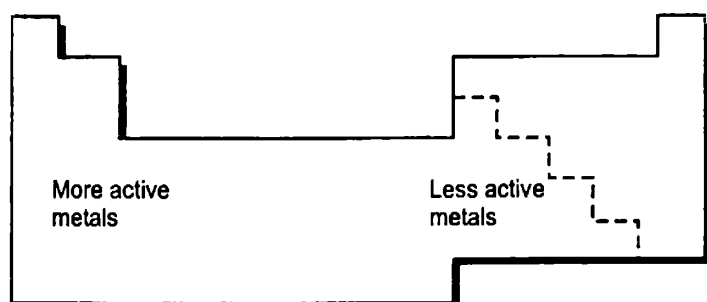


**Fig. 3.12**

Redox reactions are common for almost every element in the Periodic Table except for the noble gas elements of group VIIIA (18). In general, metals act as reducing agents, and reactive non-metals such as  $O_2$  and the halogens act as oxidizing agents as given in Fig. 3.13.

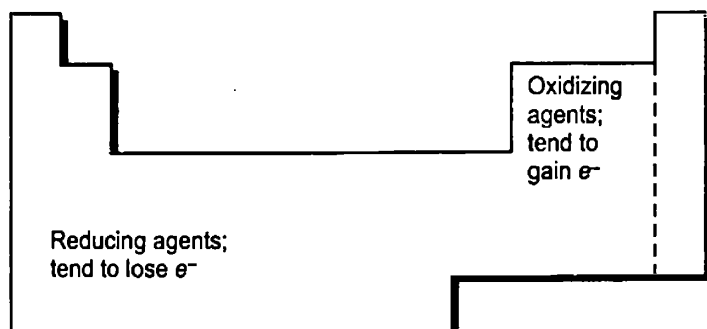
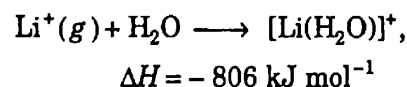


**Fig. 3.13**

## Hydration and Hydration Energy

Hydration energy is the enthalpy change that accompanies the dissolving of one mole of gaseous ions in water.



- Size of the ion and its charge determines extent of hydration.
- Greater the charge, smaller the size of the ion, greater the attraction for the lone pair of O of  $\text{H}_2\text{O}$ , hence greater the extent of hydration and hence greater the hydration energy
- size of the hydrated ions increases,
- ionic mobility decreases [heavier (hydrated) ions moves slower].

| (A) | (B) | (C) | (D) | (E) |                 | Na <sup>+</sup> | Mg <sup>2+</sup> | Al <sup>3+</sup> | Si <sup>4+</sup>                   |
|-----|-----|-----|-----|-----|-----------------|-----------------|------------------|------------------|------------------------------------|
| ↑   | ↑   | ↑   | ↑   | ↓   | Li <sup>+</sup> | →               |                  |                  | Charge on the ion (A)              |
| ↑   | ↑   | ↑   | ↑   | ↓   | Na <sup>+</sup> | ←               |                  |                  | Size of the ion (B)                |
| ↑   | ↑   | ↑   | ↑   | ↓   | K <sup>+</sup>  | →               |                  |                  | Hydration and hydration energy (C) |
| ↑   | ↑   | ↑   | ↑   | ↓   | Rb <sup>+</sup> | →               |                  |                  | Size of the hydrated ion (D)       |
| ↑   | ↑   | ↑   | ↑   | ↓   | Cs <sup>+</sup> | ←               |                  |                  | Ionic mobility (E)                 |

(Min. → Max.)                      (arrow points min. to max.)

Table 3.6 compares extent of hydration and other related properties of 1(IA) group cations.

Table 3.6 Hydration and Ionic Mobilities

| Ion             | Ionic radius (Å) | Ionic mobilities* | Radius of hydrated ion (Å) | Hydration energy**<br>$\Delta H^\circ_{\text{hyd.}}$ | Oxidation energy** $\Delta H^\circ_{\text{ox.}}$ | $E^\circ_{\text{redn.}}$ (V) |
|-----------------|------------------|-------------------|----------------------------|------------------------------------------------------|--------------------------------------------------|------------------------------|
| Li <sup>+</sup> | 0.76             | 33.5              | 3.40                       | -544                                                 | 169                                              | - 3.045                      |
| Na <sup>+</sup> | 1.02             | 43.5              | 2.76                       | -435                                                 | 208                                              | - 2.714                      |
| K <sup>+</sup>  | 1.38             | 64.5              | 2.32                       | -352                                                 | 191                                              | - 2.925                      |
| Rb <sup>+</sup> | 1.52             | 67.5              | 2.28                       | -326                                                 | 200                                              | - 2.925                      |
| Cs <sup>+</sup> | 1.67             | 68.0              | 2.28                       | -293                                                 | 196                                              | - 2.923                      |

\* Values in  $10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$

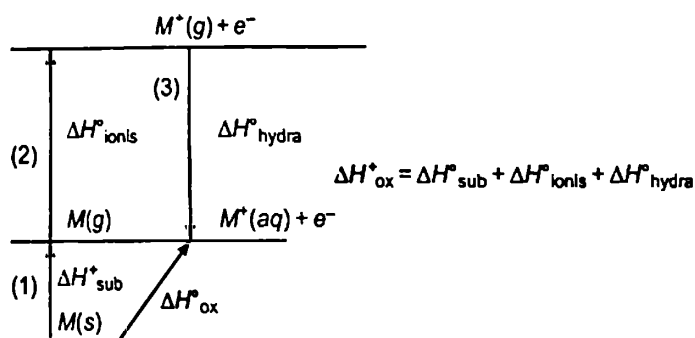
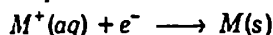
\*\* Values in kJ mol<sup>-1</sup>

- Oxidation of an alkali metal  $M$  to ions  $M^+(aq)$  involves the **hypothetical** steps :

1. Sublimation of the solid metal to the gaseous state,  $M(g)$ ,
2. Ionisation of the gaseous metal to the gaseous metal ions,  $M^+(g)$ ,
3. Hydration of the gaseous metal ions to produce  $M^+(aq)$ .

### DEEP Focus

From Table 3.6 we see that they are positive quantities, but the value is smallest for Li. This is primarily because of the less negative  $\Delta H$  for the hydration of  $Li^+$ . Thus, it appears that  $Li(s)$  should be easiest to oxidise of the alkali metal and is thus best reducing agent of the alkali metals but in aqueous solution which is also confirmed by its most negative value of  $E_{red}^*$  (standard reduction potential) of



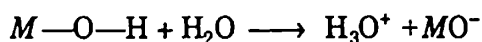
## Acid-Base Character of Oxides

On moving across a period, the basic character of the oxides gradually changes first into amphoteric and finally into acidic character.

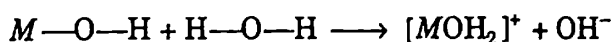
- On moving down the group, reverse behaviour is observed, i.e., from more acidic to more basic.

Oxides of the element  $M$  in  $H_2O$  produce  $MOH$

- If electronegativities difference of  $M$  and  $O$  is greater than that of  $H$  and  $O$  in  $H_2O$  then  $MOH$  is acidic due to formation of  $H_3O^+$



- If electronegativities difference of  $M$  and  $O$  is less than that of  $H$  and  $O$  in  $H_2O$  then  $MOH$  is basic due to formation of  $OH^-$



- Stability of oxides decreases across a period.
- Behaviour of the elements is shown in Fig. 3.14.

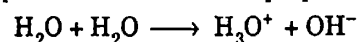
| Increasing acidic character $\longrightarrow$ |            |              |             |             |             |              |
|-----------------------------------------------|------------|--------------|-------------|-------------|-------------|--------------|
| IA<br>(1)                                     | IIA<br>(2) | IIIA<br>(13) | IVA<br>(14) | VA<br>(15)  | VIA<br>(16) | VIIA<br>(17) |
| $Li_2O$                                       | $BeO$      | $B_2O_3$     | $CO_2$      | $N_2O_5$    |             | $F_2O$       |
| $Na_2O$                                       | $MgO$      | $Al_2O_3$    | $SiO_2$     | $P_4O_{10}$ | $SO_3$      | $Cl_2O_7$    |
| $K_2O$                                        | $CaO$      | $Ga_2O_3$    | $GeO_2$     | $As_2O_5$   | $SeO_3$     | $Br_2O_7$    |
| $Rb_2O$                                       | $SrO$      | $In_2O_3$    | $SnO_2$     | $Sb_2O_5$   | $TeO_3$     | $I_2O_7$     |
| $Cs_2O$                                       | $BaO$      | $Tl_2O_3$    | $PbO_2$     | $Bi_2O_5$   | $PoO_3$     | $At_2O_7$    |

### DEEP Focus

- Oxides of the following elements are **amphoteric**

$H, Be, Al, Ga, In, Tl, Sn, Pb, Sb, Bi, Po$

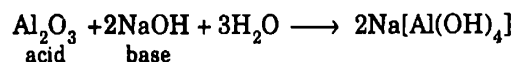
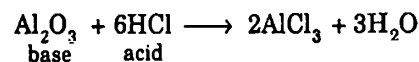
$H_2O$  is amphoteric (also called amphiprotic)



since it is  $H^+$  acceptor (base) as well as  $H^+$  donor (acid).

$BeO, Al_2O_3, SnO_2, PbO_2, \dots$  are **amphoteric** since they form

salts with acid as well as with base



- oxide is acidic if it reacts with a base.
- oxide is basic if it reacts with an acid.

| IA (1)        |                   |                                |                               |                                |                                |
|---------------|-------------------|--------------------------------|-------------------------------|--------------------------------|--------------------------------|
|               | Li                | Na                             | K                             | Rb                             | Cs                             |
| normal oxides | Li <sub>2</sub> O | Na <sub>2</sub> O              | K <sub>2</sub> O              | Rb <sub>2</sub> O              | Cs <sub>2</sub> O              |
| peroxides     | Li <sub>2</sub> O | Na <sub>2</sub> O <sub>2</sub> | K <sub>2</sub> O <sub>2</sub> | Rb <sub>2</sub> O <sub>2</sub> | Cs <sub>2</sub> O <sub>2</sub> |
| superoxides   |                   | NaO <sub>2</sub>               | KO <sub>2</sub>               | RbO <sub>2</sub>               | CsO <sub>2</sub>               |

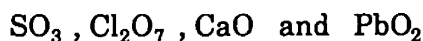
| IIA (2) |     |     |                  |                  |                  |
|---------|-----|-----|------------------|------------------|------------------|
|         | Be  | Mg  | Ca               | Sr               | Ba               |
|         | BeO | MgO | CaO              | SrO              | BaO              |
|         |     |     | CaO <sub>2</sub> | SrO <sub>2</sub> | BaO <sub>2</sub> |

|                |    |                   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|----------------|----|-------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 1              |    |                   |    |    |    |    |    |    |    |    |    |    |    |    |    |    | 18 |
| H <sup>+</sup> | 2  |                   |    |    |    |    |    |    |    |    |    | 13 | 14 | 15 | 16 | 17 |    |
| Li             | Be | Transition metals |    |    |    |    |    |    |    |    |    | B  | C  | N  | O  | F  |    |
| Na             | Mg | 3                 | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | Al | Si | P  | S  | Cl |    |
| K              | Ca | Sc                | Ti | V  | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br |    |
| Rb             | Sr | Y                 | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I  |    |
| Cs             | Ba | La                | Hf | Ta | W  | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At |    |
| Fr             | Ra | Ac                |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |

- ☐ Predominantly base oxides
- ☐ Acidic, covalent oxides
- ☐ Oxides with amphoteric nature generally ionic

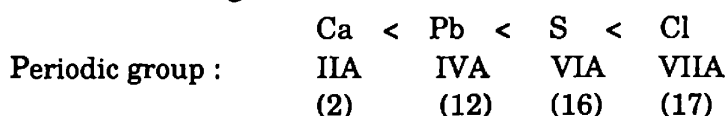
Fig. 3.14 The nature of oxides of the elements

**Illustration 1** Arrange the following oxides in order of increasing molecular (acidic) character:

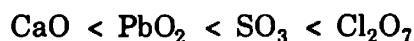


**Solution** Acidic character of oxides increases as non-metallic character of the element that is combined with oxygen increases

increasing non-metallic character

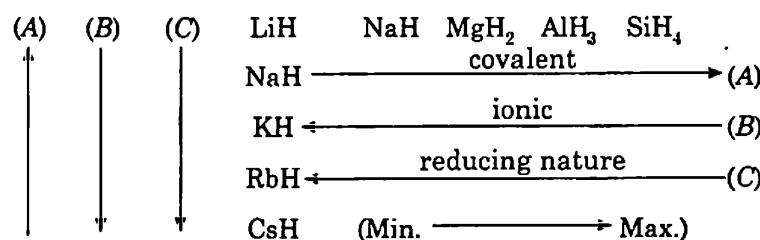


increasing (molecular) acidic character



## Hydrides

- Hydrogen combines with a number of other elements including metals and non-metals to form compounds called hydrides (with  $\text{H}^-$ ).
- Covalent nature of hydrides increases across a period and decreases down the group.
- Ionic hydride are better reducing agents than covalent hydride and reducing nature of hydride decreases across a period and increases down the group.
- Covalent and ionic hydrides are classified in Fig. 3.15.



| IA | IIA | IIIB | IVB | VB | VIB | VIIIB | VIII | IB | IIB | IIIA | IVA | VA | VIA | VIIA | VIIIA |
|----|-----|------|-----|----|-----|-------|------|----|-----|------|-----|----|-----|------|-------|
| 1  | 2   |      |     |    |     |       |      |    |     | 13   | 14  | 15 | 16  | 17   | 18    |
| H  | He  |      |     |    |     |       |      |    |     | B    | C   | N  | O   | F    |       |
| Li | Be  |      |     |    |     |       |      |    |     | Al   | Si  | P  | S   | Cl   |       |
| Na | Mg  | 3    | 4   | 5  | 6   | 7     | 8    | 9  | 10  | 11   | 12  | Ga | Ge  | As   | Se    |
| K  | Ca  | Sc   | Ti  | V  | Cr  | Mn    | Fe   | Co | Ni  | Cu   | Zn  | In | Sn  | Sb   | Te    |
| Rb | Sr  | Y    | Zr  | Nb | Mo  | Tc    | Ru   | Rh | Pd  | Ag   | Cd  | Tl | Pb  | Bi   | Po    |
| Cs | Ba  | La   | Hf  | Ta | W   | Re    | Os   | Ir | Pt  | Au   | Hg  | Pt | Pb  | Bi   | Po    |
| Fr | Ra  | Ac   |     |    |     |       |      |    |     |      |     |    |     |      |       |

- ☐ Mainly ionic with often of uncertain formula :
- ☐ Covalent, molecular structures fixed formula
- ☐ absorbed into metal lattice

Fig. 3.15 The nature of hydrides of the elements

## Melting Points and Boiling Points

A solid melts when the forces holding its constituent units in position is overcome by thermal energy as a consequence of increase in temperature. The melting temperature is determined by a number of different factors :

- (1) Nature of packing of the atoms, ions or molecules,
- (2) The lattice energy,
- (3) Association through hydrogen bond, etc.

Boiling involves complete detachment of the particles of a liquid. Both the melting and boiling points of an element thus indicate the nature and extent of bonding between the atoms of that element. In spite of the contribution of a large number of variable factors controlling the melting and boiling points, a striking periodicity is observed in their values. Fig. 3.16

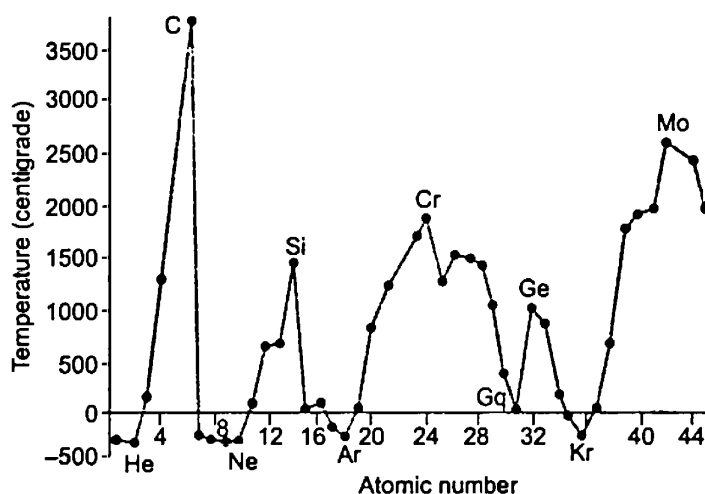


Fig. 3.16 Periodic variation of melting point of elements

The graph represents a plot of melting points of some elements against their respective atomic numbers. The shape of the curve indicates periodic variation. It may be further observed that :

- The noble gases have very low melting points.
- The melting point of the elements in any period increases gradually to group 14 where it bears a maximum; it then decreases to the next noble gas.
- The melting points of elements occurring in a period usually decrease downwards, i.e., as the elements bear higher atomic numbers.



### DEEP Focus

- (i) The noble gas atoms contain a completed electron shell. So there exists little tendency for these atoms to combine between themselves. This is why they occupy the lowest range of melting points.
- (ii) The alkali metals have only one electron in their outermost shells. Their contribution to metallic bonding is, therefore, weak, resulting in low melting points.
- (iii) As the number of electrons participating in metallic bonding increases, the melting point also increases:  $\text{Be} > \text{Li}$ ;  $\text{Mg} > \text{Na}$ .
- (iv) Boron, carbon and silicon form giant three-dimensional structures; breaking of these arrangements require large amount of energy. Hence, they have very high melting points.
- (v) Nitrogen, oxygen, fluorine—all form stable diatomic molecules containing triple, double and single bonds (between their atoms) respectively. They do not form giant three-dimensional lattices—may be due to greater repulsion between the non-bonding electrons and the greater stabilities of these multiple bonds. At the same time, very poor binding exists among the molecules themselves. Consequently they have very low melting points.
- (vi) As we proceed downwards along a group, the elements involve increasingly highly orbital for binding their atoms. Poorer bonding, therefore, results in lowering of melting point ( $\text{Li}-\text{Na}-\text{K}-\text{Rb}-\text{Cs}$ ). Exceptions to this take place in group 15 to 17 (e.g.,  $\text{P} > \text{N}$ ;  $\text{S} > \text{O}$ ;  $\text{I} > \text{Br} > \text{Cl} > \text{F}$ ). Phosphorus and sulphur have a diminished tendency to bond multiplicity (larger size poor lateral overlap). They form single bonded polyatomic structures having higher melting points. Among the halogens, polarisability of the halogen atoms increases with their size; stronger van der Waals' interaction is established, resulting in gradually higher melting point. Thus bromine is a liquid and iodine is a solid at room temperature.

The variation of melting point along a transition series is irregular. The  $d$ -orbitals and the electrons there in contribute to metallic bonding to a varying degree. A sharp drop in melting point is observed just after the completion of a transition series, e.g.,  $\text{Cu} : 1356 \text{ K}$  vs.  $\text{Zn} : 692.5 \text{ K}$ ;  $\text{Ag} : 1233.8 \text{ K}$  vs.  $\text{Cd} : 593.9 \text{ K}$ . It appears that the completed  $d$ -orbitals do no longer effectively participate in metallic bonding.

## Density

The densities of the elements in the solid state also exhibit periodic variation when plotted against their atomic numbers. It may be observed from Fig. 3.17 that the densities of the alkali metals occupy the minima in the curve; the density first rises and then decreases along a period, the elements in the middle having the highest density values.

Here again the underlying reason is largely complicated by the nature of packing of the atoms. A simple interpretation may be provided by remembering that **stronger and compact binding leads to high density**. The binding force is again dependent on the number of valence electrons provided by each

atom. This is why the density of the central elements in any period is highest.

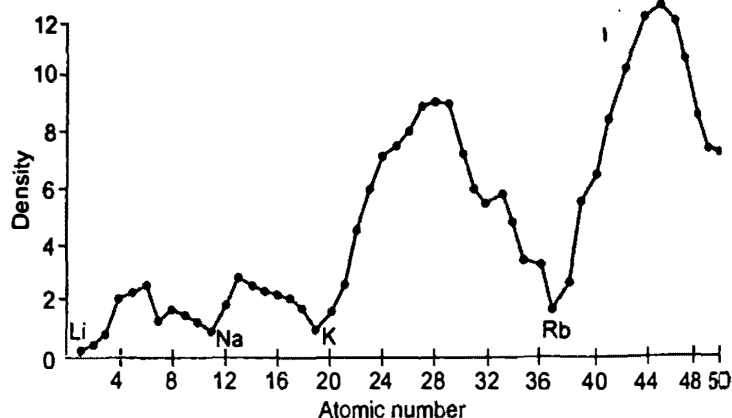


Fig. 3.17 Periodic variation of density with atomic number

The increase of density down any group in the Periodic Table is similarly explained from the increasing number of neutrons and protons in the nuclei.

## Atomic Volume

Lothar Meyer, in 1870, independently introduced the idea of periodicity in properties of the elements from study of their atomic volumes. **The atomic volume is the volume of one mole of atoms of an element; it was obtained as atomic volume ( $\text{cc mol}^{-1}$ ) = atomic weight/density**. This is only a rough indication of atomic size since the density of an element is determined by several factors like physical state, allotropic form, number of atoms per molecule, nature of packing and so on. Yet a periodic variation is obtained when the atomic volumes of elements are plotted against their atomic numbers. (Fig. 3.18)

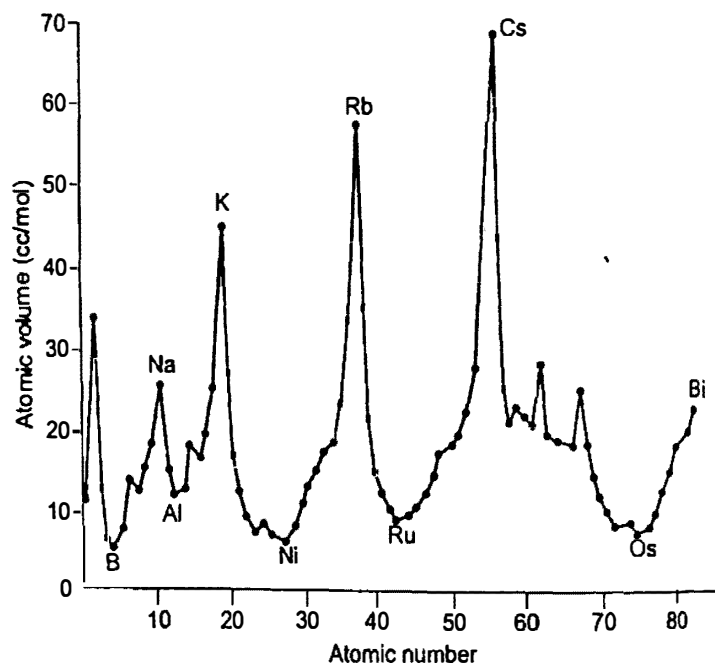


Fig. 3.18 Periodic variation of atomic volume

## Target Practice 3

- Any salt  $MCl_2$  is soluble in water. Relate lattice energy and hydration energy for  $MCl_2$  to be water soluble .....
- Arrange hydroxide of alkaline earth metals in increasing solubility in water. ....
- Arrange solubility of sulphates of
  - alkali metals
  - alkaline earth metals
 in increasing order .....
- Which is more stable (thermally) in each pair
  - $BaCO_3, SrCO_3$
  - $BeCO_3, CaCO_3$
  - $MgCO_3, BeCO_3$
  - $Na_2CO_3, Li_2CO_3$
  - $NaHCO_3, Na_2CO_3$
- What is enthalpy change in the formation of  $MgO$ ?
  - $Mg(s) \longrightarrow Mg(g)$  ;  $\Delta H = S$
  - $Mg(g) \longrightarrow Mg^+(g) + e^-$  ;  $\Delta H = I_1$
  - $Mg^+(g) \longrightarrow Mg^{2+}(g) + e^-$  ;  $\Delta H = I_2$
  - $O_2(g) \longrightarrow 2O(g)$  ;  $\Delta H = D$
  - $O(g) + e^- \longrightarrow O^-(g)$  ;  $\Delta H = -E_1$
  - $O^-(g) + e^- \longrightarrow O^{2-}(g)$  ;  $\Delta H = E_2$
  - $Mg^{2+}(g) + O^{2-}(g) \longrightarrow MgO(s)$  ;  $\Delta H = -U$

### Answers

- For a salt to be water soluble, hydration energy should exceed the lattice energy  

$$\text{hydration energy} > \text{lattice energy}$$
- $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$   
 For salts of small anions (as fluorides, hydroxides), the lattice energy decreases from Be to Ba due to increase in size. Hydration energy also decrease but this decrease is less than decrease in lattice energy. As a result hydration energy increases. Hence, solubility of hydroxides increases.
- $Li_2SO_4 < Na_2SO_4 < K_2SO_4 < Rb_2SO_4$
  - $BaSO_4 < CrSO_4 < CaSO_4 < MgSO_4 < BeSO_4$
- $BaCO_3 > SrCO_3$
  - $CaCO_3 > BeCO_3$
  - $MgCO_3 > BeCO_3$
  - $Na_2CO_3 > Li_2CO_3$
  - $Na_2CO_3 > NaHCO_3$
- Add all steps (i) to (vii) (with (iv)/2)
 
$$Mg(s) + \frac{1}{2} O_2(g) \longrightarrow MgO(s)$$

Net enthalpy change is

$$\Delta H = S + I_1 + I_2 + \frac{D}{2} - E_1 + E_2 - U$$

## Practice Exercise 3

- Which has greater (EA) value in each pair?
  - F or  $Cl^-$
  - O or  $O^-$
  - Ne<sup>+</sup> or F
  - F or  $F^-$
- EA of Cu is  $123 \text{ kJ mol}^{-1}$  but that of Zn is  $-87 \text{ kJ mol}^{-1}$ . Explain.
- We consider formation of  $NaCl(s)$  using Born-Haber cycle which involves following steps :
 

|       |                                                    |                          |
|-------|----------------------------------------------------|--------------------------|
| (I)   | $Na(s) + \frac{1}{2} Cl_2 \longrightarrow NaCl(s)$ | $\Delta H = Q$           |
| (II)  | $Na(s) \longrightarrow Na(g)$                      | $\Delta H = S$           |
| (III) | $Na(g) \longrightarrow Na^+(g) + e^-$              | $\Delta H = I$           |
| (IV)  | $\frac{1}{2} Cl_2(g) \longrightarrow Cl(g)$        | $\Delta H = \frac{D}{2}$ |
| (V)   | $Cl(g) + e^- \longrightarrow Cl^-(g)$              | $\Delta H = ?$           |
| (VI)  | $Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$        | $\Delta H = -U$          |

Can you derive value of (EA) of  $Cl(g)$  atom.
- Why are the electron affinities of the alkaline earth metals positive?
- Is it likely that Ar will form the anion  $Ar^-$ .
- Considering their electrons affinities, do you think it is possible for alkali metals to form an anion like  $M^-$  where  $M$  represents an alkali metal.
- What is relationship between the electron affinity of a univalent cation such as  $Na^+$  and the ionisation energy of the neutral atom?
- Calculate effective nuclear charge that added electron would experience in F-atom in the formation of negative ion.
- Explain  $Na_2CO_3$  is thermally stable, but  $Li_2CO_3$  and  $MgCO_3$  both decompose on heating.
  - $BeCl_2$  and  $AlCl_3$  are Lewis acids.
  - B and Si resemble each other in their properties.
- Which is more electronegative in each pair?
  - $F^-$  or  $Na^+$
  - Ne or  $F^-$
  - F or Cl
  - $H^-$  or He
- Electronegativity of F on Pauling's scale is 4.0. What is the value on Mulliken's scale?
- $A^+B^-$  and  $A^-B^+$  can be formed from elements (A) and (B). Explain their formation based on relative values of (EN), (EA) and (IE).
- Covalent radius of F is  $0.72 \text{ \AA}$ . Calculate its Allred-Rochow's electronegativity.
- Covalent radius of oxygen is  $0.74 \text{ \AA}$  and its A.R. electronegativity is 3.5. What is effective nuclear charge experienced by oxygen?
- Make a **Born-Haber** cycle for the preparation of  $MgBr_2(s)$ .
- Calculate the electronegativity of carbon from the following data :
 
$$E_{H-H} = 104.2 \text{ kcal mol}^{-1}; \quad E_{C-C} = 83.1 \text{ kcal mol}^{-1}$$

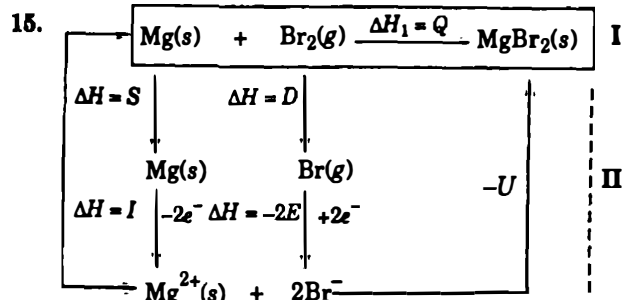
$$E_{C-H} = 98.8 \text{ kcal mol}^{-1}$$

17. (IE) and (EA) of fluorine are respectively 17.418 eV and -9.278 eV. Calculate (EN) of fluorine atom.
18. Four atoms are arbitrarily labelled *D*, *E*, *F* and *G*. Their electronegativities are as follows *D* = 3.8, *E* = 3.3, *F* = 2.8 and *G* = 1.3. If the atoms of these elements form the molecules *DE*, *DG*, *EG*, and *DF*, how would you arrange these molecules in order of increasing covalent bond character.
19. Tendency to lose electrons shows reducing property of the element. Arrange the following in order of reducing property:  
 (a) Na, K, Rb (b) Na, Mg, Al  
 (c) F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> (d) Mg, Ca, Sr
20. Li is better reducing agent than Na. Explain.
21. Which of the following reactions are possible?  
 (a)  $3\text{Mg} + 2\text{Al}^{3+} \longrightarrow 2\text{Al} + 3\text{Mg}^{2+}$   
 (b)  $\text{Cl}_2 + 2\text{I}^- \longrightarrow \text{I}_2 + 2\text{Cl}^-$   
 (c)  $\text{K}^+ + \text{Na} \longrightarrow \text{K} + \text{Na}^+$
22. Arrange the following ions in increasing Na<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>  
 (i) extent of hydration  
 (ii) hydration energy  
 (iii) size of the hydrated ions  
 (iv) ionic mobility  
 (v) standard reduction potential ( $E^\circ_{\text{redn.}}$ ),  
 $\text{M}^{n+}(\text{aq}) + ne^- \longrightarrow \text{M}(\text{s})$   
 (vi) enthalpy of oxidation ( $\Delta H^\circ_{\text{ox}}$ ) of *M*(s).
23. In the preparation of hydrocarbon by Kolbe's electrolysis, generally RCOONa or RCOOK are taken but not RCOOLi. Explain.
24. LiCl is hydrated but NaCl is always anhydrous. Explain.
25. Arrange NH<sub>3</sub>, PH<sub>3</sub> and AsH<sub>3</sub> in increasing reducing nature.
26. Fill in the blanks :  
 (i) NaH is ..... hydride.  
 (ii) B<sub>2</sub>H<sub>6</sub> is called .....  
 (iii) SiH<sub>4</sub> is called .....  
 (iv) Most widely used mixed hydride in organic synthesis is .....
27. Write the formulae and names of the hydride of the following second period elements :  
 Li, C, N, O, F.
28. SnO<sub>2</sub> forms two types of colloidal sols, positively charged in an acidic medium and negatively charged in a basic medium. Explain.
29. Arrange following oxides in increasing acidic nature  
 Li<sub>2</sub>O, BeO, B<sub>2</sub>O<sub>3</sub>
30. Explain:  
 (i) Aqueous CO<sub>2</sub> can cause rusting.  
 (ii) Al<sub>2</sub>O<sub>3</sub> is amphoteric while B<sub>2</sub>O<sub>3</sub> is acidic.  
 (iii) BeO and Al<sub>2</sub>O<sub>3</sub> both are amphoteric.
31. Which oxide is more basic, MgO or BaO? Why?
32. Write the formulae and names of the oxides of second-period elements (Li to N). Identify the oxides as acidic, basic or amphoteric.

## Answers

1. (i) F (ii) O<sup>-</sup> (more positive) (iii) Ne<sup>+</sup> (iv) F
2.  $\text{Cu}(\text{Ar}) 3d^{10} 4s^1 + e^- \longrightarrow \text{Cu}^-(\text{Ar}) 3d^{10} 4s^2$   
 In case of Cu, added electron goes into empty 4s-orbital where it can get repulsion to a certain extent giving a positive value of (EA). In case of Zn, added electron can be accommodated into 4p-orbital giving a negative value of (EA).
3. (v) involves addition of electron to Cl(g)  
 $\text{Cl}(\text{g}) + e^- \longrightarrow \text{Cl}^-(\text{g}) \quad EA = x$   
 Energy released is (EA)  
 Adding (ii) to (vi) gives  
 $\text{Na}(\text{s}) + \frac{1}{2} \text{Cl}_2(\text{g}) \longrightarrow \text{NaCl}(\text{s})$   
 which is also the step (i), hence  
 $S + I + \frac{D}{2} + x(EA) - U = Q$   
 hence, *x* is calculated.
4.  $\text{M}(\text{g}) + e^- \longrightarrow \text{M}^-(\text{g})$   
 The extra electron must enter *np*-subshell, which is effectively shielding the two *ns*-electrons and the inner electrons. Consequently, the alkaline earth metals have little tendency to pick up an extra electron.
5. Added electron enters 4s orbital of higher energy where it gets repulsion. Thus, (EA) value is positive. Thus, Ar<sup>-</sup> is not formed.
6.  $\text{M}(\text{g}) + e^- \longrightarrow \text{M}^-(\text{g}) \quad \Delta H = -ve$   
 $\begin{array}{ccc} ns^1 & & ns^2 \\ \uparrow & & \uparrow \downarrow \end{array}$   
 Yes, since M<sup>-</sup>(g) has paired *ns*-electrons
7.  $\text{Na}^+(\text{g}) + e^- \longrightarrow \text{Na}(\text{g}) \quad \Delta H = -(EA)$   
 $\text{Na}(\text{g}) \longrightarrow \text{Na}^+(\text{g}) + e^- \quad \Delta H = +(IE)$   
 $\therefore (IE) = -(EA)$
8.  $Z^* = Z - S = 5.85$
9. (i) Due to diagonal relationship, Li and Mg resemble.  
 (ii) Due to diagonal relationship.  
 (iii) Due to diagonal relationship.
10. (a) both zero (b) both zero (c) F (d) both zero
11. 11.2 (4.8 times larger)
12.  $A \longrightarrow A^+ + e^-$  if  $(IE)_A < (IE)_B$   
 $B + e^- \longrightarrow B^-$  if  $(EA)_A < (EA)_B$   
 Thus, A<sup>+</sup>B<sup>-</sup> is formed if  $(IE)_A + (EA)_A < (IE)_B + (EA)_B$   
 or  $\frac{(IE)_A + (EA)_A}{2} < \frac{(IE)_B + (EA)_B}{2}$   
 or  $(EN)_A < (EN)_B$   
 Thus, A<sup>+</sup>B<sup>-</sup> exists if electronegativity of A < B. Similarly, A<sup>-</sup>B<sup>+</sup> is formed if electronegativity of A > B.

13. 4.7952    14. 4.2039



$$\Delta H_{II} = S + I + D - 2E - U = \Delta H_1 = Q$$

$S$  = heat of sublimation of  $\text{Mg(s)}$

$I$  = ionisation energy of  $\text{Mg(g)}$

$D$  = dissociation energy of  $\text{Br}_2(\text{g})$

$-E$  = electron affinity of  $\text{Br(g)}$

$-U$  = lattice energy of  $\text{MgBr}_2(\text{s})$

$Q$  = heat of formation of  $\text{MgBr}_2(\text{s})$

16. Using Pauling's scale :

$$\chi_{\text{C}} = \chi_{\text{H}} + 0.182\sqrt{\Delta_{\text{C-H}}}$$

$$\chi_{\text{H}} = 2.05$$

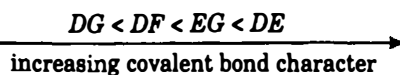
$$\Delta_{\text{C-H}} = E_{\text{C-H}} - \sqrt{E_{\text{H-H}} \cdot E_{\text{C-C}}}$$

$$= 98.8 - \sqrt{104.2 \times 83.1} = 5.75$$

$$\chi_{\text{C}} = 2.49$$

17. 4.07 eV

18. Smaller the (EN) difference, larger the covalent nature.



19. (a)  $\text{Na} < \text{K} < \text{Rb}$  (b)  $\text{Na} > \text{Mg} > \text{Al}$  (c)  $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$   
(d)  $\text{Mg} < \text{Ca} < \text{Sr}$

20. The large hydration energy is responsible for the case with which lithium ion will be made in solution. The electrode potential of Li reflects this tendency for Li to convert into hydrated ion, rather than its inherent ability as a reducing agent. If lithium takes part in reactions that do not involve water, then it does show less reducing power than the other members of the group.

21. (a) and (b)

22. (i)  $\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$ , (ii)  $\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$

(iii)  $\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$ , (iv)  $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+$

(v)  $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+$  ( $E_{\text{red}}^\circ = -ve$ ), (vi)  $\text{Al} < \text{Mg} < \text{Na}$

23. Ionic mobility of  $\text{Li}^+ \ll \text{Na}^+$  or  $\text{K}^+$  (Refer Table 3.6)

Thus,  $\text{Na}^+$  or  $\text{K}^+$  reaches cathode faster than  $\text{Li}^+$  and thus is discharged at a faster rate. (This is due to greater hydration of  $\text{Li}^+$  than other ions)

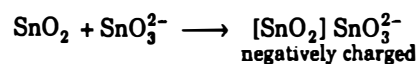
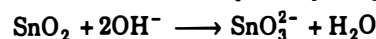
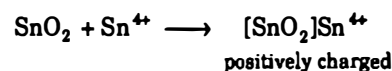
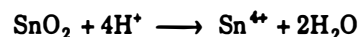
24.  $\text{Li}^+$  (smaller size) is more hydrated than  $\text{Na}^+$  (larger size).

25.  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3$

26. (i) an ionic (ii) diborane (iii) silane (iv)  $\text{LiAlH}_4$

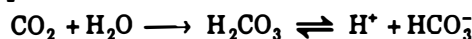
27.  $\text{LiH}$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{HF}$

28.  $\text{SnO}_2$  forms  $\text{Sn}^{4+}$  in acidic medium and  $\text{SnO}_3^{2-}$  in basic medium. These ions are preferentially adsorbed on  $\text{SnO}_2$  forming colloidal sol.

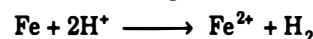


29.  $\text{Li}_2\text{O} < \text{BeO} < \text{B}_2\text{O}_3$   
basic    amphoteric    acidic

30. (i)  $\text{CO}_2$  is an acidic oxide



$\text{H}^+$  can react with Fe forming  $\text{Fe}^{2+}$  and thus cause rusting.



(ii) While going down the group, basic nature increases and acidic nature decreases, hence

$\text{B}_2\text{O}_3$  is an acidic oxide.

$\text{Al}_2\text{O}_3$  is an amphoteric oxide.

(iii) Due to diagonal relationship.

31.  $\text{BaO}$

32.  $\text{Li}_2\text{O}$             basic  
 $\text{BeO}$             amphoteric

$\text{B}_2\text{O}_3$             acidic

$\text{CO}_2$             acidic

$\text{N}_2\text{O}_5$             acidic

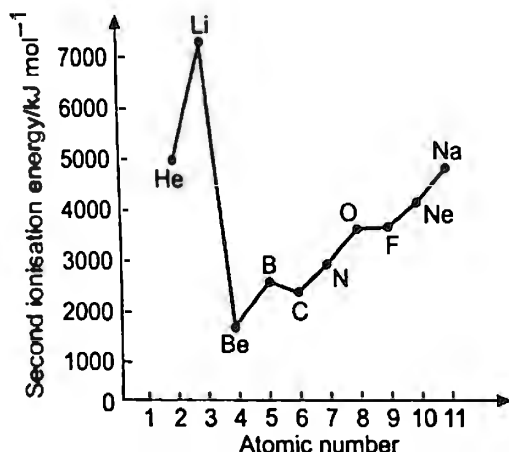
# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** Draw a graph that shows how the second (IE) (given in  $\text{kJ mol}^{-1}$ ) of the elements helium to sodium change. Explain the shape of the graph.

|                   | He  | Li  | Be  | B   | C   | N   | O   | F   | Ne  | Na  |
|-------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| (IE) <sub>2</sub> | 525 | 729 | 175 | 242 | 235 | 285 | 333 | 347 | 395 | 456 |
|                   | 0   | 8   | 7   | 7   | 3   | 6   | 8   | 1   | 2   | 2   |

**Solution** Once Li has lost an electron, it has noble gas electron structure, i.e., a filled set of electron shells. Like the noble gas it has high (IE)<sub>2</sub>. When Be has lost one electron, it is isoelectronic of Li. Its single outer electron is shielded from the nucleus by a filled shell of electron. This gives a low (IE)<sub>2</sub>. In similar fashion, there is a trend upwards across the period, with dips at places when an electron is outside a filled s-orbital, or where two electrons begin to fill a single p-orbital. Thus, behaviour of nonvalent cation (formed after one electron is lost) with atomic number Z, is just parallel to the atom with atomic number (Z - 1).



A graph of second ionisation energy against atomic number for the elements helium to sodium

| For (IE) <sub>2</sub> behaviour is similar to | He <sup>+</sup> | Li <sup>+</sup> | Be <sup>+</sup> | B <sup>+</sup> | C <sup>+</sup> | N <sup>+</sup> | O <sup>+</sup> | F <sup>+</sup> | Ne <sup>+</sup> | Na <sup>+</sup> |
|-----------------------------------------------|-----------------|-----------------|-----------------|----------------|----------------|----------------|----------------|----------------|-----------------|-----------------|
| →                                             | H               | He              | Li              | Be             | B              | C              | N              | O              | F               | Ne              |

**Problem 2.** Of the following pairs, which would you expect to have

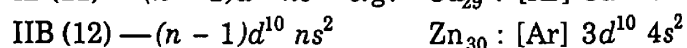
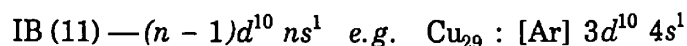
- the lower first (IE), Sr or Be?
- the more non-metallic behaviour, Ga or P?
- the larger atomic radius, Mg or Sr?
- the more negative (EA), Br or I?

**Solution** In the Periodic Table (IE), (EA) and non-metallic behaviour decrease down the group and increase across a period while radius increases down the group and decreases along a period.

- Sr has a lower (IE) than Be.
- P has more non-metallic behaviour than Ga.
- Sr has larger atomic radius than Mg.
- Br has more (EA) than I.

**Problem 3.** In the modern Periodic Table, the elements in groups IB(11) and IIB(12) are shown in d-block. This block is the place where the transition elements are found. Why do you think some chemists argue that the Group IB(11) and IIB(12) elements should not be considered as d-block elements?

**Solution** In the d-block, the 3d, 4d, or 5d orbitals are being filled. The properties of the transition elements are a result of their having unfilled d-orbitals. However IB and IIB elements have full d-orbitals.



Indeed, these elements have s-orbitals filling. This is one reason why some chemists think them misplaced tacked on the end of the transition elements. However, the chemical properties of the IB metals make to include them among the transition metals, viz.,  $\text{Cu}^{2+}$  is coloured, forms complexes etc. The IIB metals are best excluded.

**Problem 4.** There are certain exceptions to the properties of the elements.

- Which metal is liquid at room temperature?
- Which non-metal is a solid with an extremely high melting point?
- Which non-metal is a liquid at room temperature?
- Which two elements would you expect to combine in the most violent fashion?

**Solution** (i) Hg

(ii) Carbon (diamond or graphite)

(iii) Br

(iv) Cs and F

**Problem 5.** The heats of formation ( $\Delta H_f^\circ$ ) of the oxides of the third period, sodium to chlorine, are in  $\text{kJ mol}^{-1}$

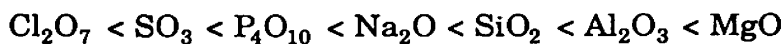
|                   |      |                                |                  |                                |                 |                                |
|-------------------|------|--------------------------------|------------------|--------------------------------|-----------------|--------------------------------|
| Na <sub>2</sub> O | MgO  | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | P <sub>4</sub> O <sub>10</sub> | SO <sub>3</sub> | Cl <sub>2</sub> O <sub>7</sub> |
| -416              | -602 | -1676                          | -911             | -2984                          | -395            | +250                           |

Divide these values by the number of oxygen atoms in the formula of the oxide. The resulting figure is a measure of the strength of the oxide. What is the link between the figures and the structures of the oxides?

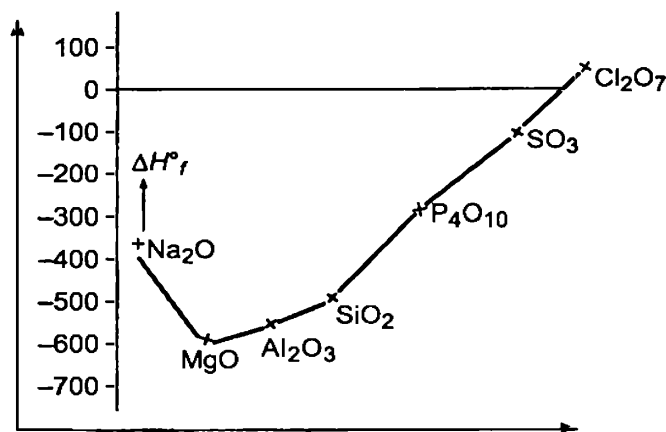
### Solution

| Oxide                          | $\Delta H_f^\circ$ (kJ mol <sup>-1</sup> ) | Number of O-atoms = $x$ | $\Delta H_f^\circ / x$ |
|--------------------------------|--------------------------------------------|-------------------------|------------------------|
| Na <sub>2</sub> O              | -416                                       | 1                       | -416                   |
| MgO                            | -602                                       | 1                       | -602                   |
| Al <sub>2</sub> O <sub>3</sub> | -1676                                      | 3                       | -558.7                 |
| SiO <sub>2</sub>               | -911                                       | 2                       | -455.5                 |
| P <sub>4</sub> O <sub>10</sub> | -2984                                      | 10                      | -298.4                 |
| SO <sub>3</sub>                | -395                                       | 3                       | -131.7                 |
| Cl <sub>2</sub> O <sub>7</sub> | +250                                       | 7                       | 35.7                   |

More negative the value of ( $\Delta H_f^\circ / x$ ), greater the stability. Thus, MgO is most stable and Cl<sub>2</sub>O<sub>7</sub> is least stable, stability being :



In general, stability decreases across the period from left to right (except Na<sub>2</sub>O). This is shown in given fig.



**Problem 6.** Match the columns in (A) with those given in (B).

| (A)                                       | (B)                           |
|-------------------------------------------|-------------------------------|
| (a) Inner transition elements             | (i) Diagonal relationship     |
| (b) <i>d</i> -block elements              | (ii) <i>p</i> -block elements |
| (c) Elements with unpaired electrons      | (iii) Typical elements        |
| (d) Be—Al                                 | (iv) Block deciding rule      |
| (e) <i>s</i> and <i>p</i> -block elements | (v) Transition elements       |
| (f) Elements of 3rd period                | (vi) Paramagnetic             |
| (g) $ns^2np^1$ to $ns^2np^5$              | (vii) Normal elements         |
| (h) Aufbau principle                      | (viii) <i>f</i> -block        |

### Solution

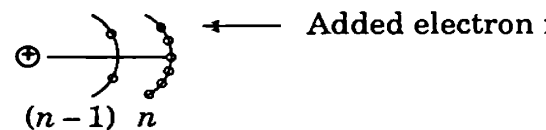
| A   | B      |
|-----|--------|
| (a) | (vi)   |
| (b) | (i)    |
| (c) | (v)    |
| (d) | (iv)   |
| (e) | (vii)  |
| (f) | (iii)  |
| (g) | (ii)   |
| (h) | (viii) |

**Problem 7.** What is effective nuclear charge at periphery of nitrogen atom when an electron is added in the formation of an anion. Consider the atom when the atom is ionised.

### Solution

$$\text{N}(7) = 1s^2 2s^2 2p^3$$

Added electron will be screened by five ( $2s^2 2p^3$ ) electrons in 2nd orbit and two ( $1s^2$ ) electrons in 1st orbit.

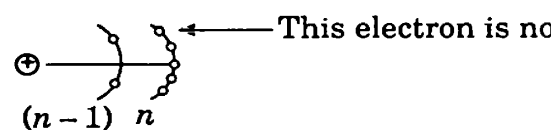


The screening constant,  $\sigma = 5 \times 0.35 + 2 \times 0.85$

$$\text{Total } \sigma = 3.45$$

$$\therefore \text{Effective nuclear charge} = 7 - 3.45$$

In the formation of positive ion, electron is removed from the outer orbit is screened by four electrons in  $n$ th orbit and two electrons in  $(n-1)$ th orbit



Screening constant,  $\sigma = 4 \times 0.35 + 2 \times 0.85$

$$\text{Total value of } \sigma = 3.1$$

$$\therefore \text{Effective nuclear charge} = 7 - 3.1$$

**Problem 8.** The sums of first and second ionization energies and those of third and fourth ionization energies (in MJ mol<sup>-1</sup>) of nickel and platinum are

|    | $(IE)_1 + (IE)_2$ | $(IE)_3 + (IE)_4$ |
|----|-------------------|-------------------|
| Ni | 2.49              | 11.36             |
| Pt | 2.66              | 11.80             |

Based on this information, write

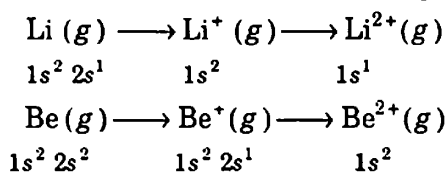
- the most common oxidation states
- name of the metal (Ni or Pt) which forms compounds in its +4 oxidation state

**Solution** (i)  $\text{Ni} = +2$ ,  $\text{Pt} = +4$  since  $(IE)_1 + (IE)_2$  of Ni is less than its  $(IE)_3 + (IE)_4$  and reverse is the case in Pt.

(ii) Platinum forms more stable complexes in +4 state due to its higher stability than +2 state.

**Problem 9.** Which atom should have a higher second  $IE$ : Li or Be?

**Solution** Ionisation of Li and Be can be represented as



Since, 1s-electrons shield 2s-electrons much more effectively than they shield each other, we predict that it should be much easier to remove a 2s electron from  $\text{Be}^+$  than to remove a 1s-electron from  $\text{Li}^+$  which has inert gas [He] configuration.

**Problem 10.** A technique called photoelectron spectroscopy is used to measure the  $IE$  of atoms. A sample is irradiated with UV light, and electrons are ejected from the valence shell. The kinetic energies of the ejected electrons are measured. Since the energy of the UV photon and the kinetic energy of the ejected electrons are known, we can write

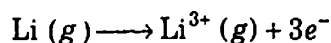
$$h\nu = (IE) + \frac{1}{2} mu^2$$

where  $\nu$  is the frequency of the UV light, and  $m$  and  $u$  are the mass and velocity of the electron, respectively. In one experiment the kinetic energy of the ejected electron from potassium is found to be  $5.34 \times 10^{-19}$  J using UV source of wavelength 162 nm. Calculate  $IE$  of potassium ( $h = 6.62 \times 10^{-34}$  J s,  $c = 3 \times 10^8$  m s $^{-1}$ ).

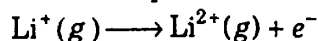
**Solution**  $h\nu = (IE) + \frac{1}{2} mu^2$

$$\begin{aligned} IE &= h\nu - \frac{1}{2} mu^2 \\ &= \frac{hc}{\lambda} - \frac{1}{2} mu^2 \\ &= \left( \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{162 \times 10^{-9}} \right) - (5.34 \times 10^{-19}) \\ &= 6.91 \times 10^{-19} \text{ J atom}^{-1} \\ &= 416.54 \times 10^3 \text{ J mol}^{-1} \\ &= 416.54 \text{ kJ mol}^{-1} \end{aligned}$$

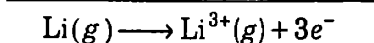
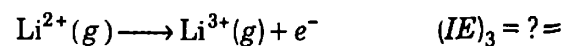
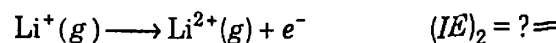
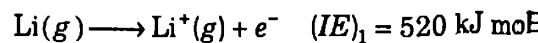
**Problem 11.** The energy needed for the following process is  $1.96 \times 10^4$  kJ mol $^{-1}$



If the first ionisation energy of lithium is 520 kJ mol $^{-1}$ , calculate the second ionisation energy of lithium, that is the energy required for the process



**Solution** Stepwise ionisation of  $\text{Li}(g)$  is written as :



$$(IE)_{\text{Total}} = 1.96 \times 10^4 \text{ kJ mol}^{-1}$$

$\text{Li}^{2+}(g)$  is isoelectronic of  $\text{H}(g)$ , hence

$$(IE)_3 = (2.18 \times 10^{-18}) (Z^2) \left( \frac{1}{n^2} \right) \text{ J atom}^{-1}$$

$$= 2.18 \times 10^{-18} \times 9 \text{ J atom}^{-1}$$

$$= 2.18 \times 10^{-18} \times 9 \times 6.02 \times 10^{23} \text{ J mol}^{-1}$$

$$\therefore y = 11.81 \times 10^3 \text{ kJ mol}^{-1}$$

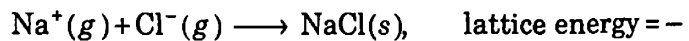
$$(IE)_{\text{Total}} = (IE)_1 + (IE)_2 + (IE)_3$$

$$1.96 \times 10^4 = 520 + x + 11.81 \times 10^3$$

$$\therefore x = (IE)_2 = 7.269 \times 10^3 \text{ kJ mol}^{-1}$$

**Problem 12.** Which has the larger lattice energy NaCl or CsCl?

**Solution** Lattice energy is defined as the energy when gaseous ions combine to form ionic solid.



The magnitude of a substance's lattice energy is affected both by the charges on its constituent ions and by the size of those ions. The higher the charges on the ions and smaller the sizes of the cations and larger the size of the anion, the larger the lattice energy.

Charges on each ion are identical.

$\text{Na}^+$  is smaller than  $\text{Cs}^+$ .

$\text{Cl}^-$  is identical

Thus, lattice energy of  $\text{NaCl} > \text{CsCl}$ .

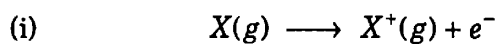
**Problem 13.**  $\frac{N_0}{2}$  atoms of  $X(g)$  are converted into

$X^+(g)$  by energy  $\Delta H_1$ .  $\frac{N_0}{2}$  atoms of  $X(g)$  are converted into

$X^+(g)$  and  $\frac{N_0}{2}$  atoms if  $X(g)$  are converted into  $X^-(g)$  by energy  $\Delta H_2$ . Calculate  $(IE)$  and  $(EA)$  of  $X(g)$ .

**Solution** Let  $(IE)$  of  $X(g) = I$  per atom

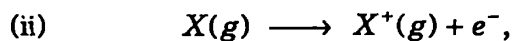
and  $(EA)$  of  $X(g) = -E$  per atom



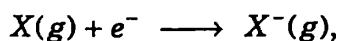
$$\text{Energy required to ionise } \frac{N_0}{2} \text{ atom of } (X)g = \frac{N_0 I}{2}$$

$$\frac{N_0 I}{2} = \Delta H_1$$

$$\therefore I = \frac{2\Delta H_1}{N_0}$$



$$\text{Energy} = \frac{N_0 I}{2} \text{ for } \frac{N_0}{2} \text{ atoms}$$



$$\text{Energy} = \frac{-N_0 E}{2} \text{ for } \frac{N_0}{2} \text{ atoms}$$

$$\therefore \quad \frac{N_0 I}{2} - \frac{N_0 E}{2} = \Delta H_2$$

$$N_0 \frac{2\Delta H_1}{2N_0} - \frac{N_0 E}{2} = \Delta H_2$$

$$\frac{-N_0 E}{2} = \Delta H_2 - \Delta H_1$$

$$-E = \frac{2(\Delta H_2 - \Delta H_1)}{N_0}$$

$$\therefore \text{ Ionisation Energy (IE)} = \frac{2\Delta H_1}{N_0} \text{ atom}^{-1},$$

$$\begin{aligned} & \text{Electron Affinity (EA)} \\ &= \frac{2(\Delta H_2 - \Delta H_1)}{N_0} \text{ atom}^{-1} \end{aligned}$$

**Problem 14.** Calculate the electronegativity of fluorine from the following data :

$$E_{H-H} = 104.2 \text{ kcal mol}^{-1}$$

$$E_{F-F} = 36.6 \text{ kcal mol}^{-1}$$

$$E_{H-F} = 134.6 \text{ kcal mol}^{-1}$$

Electronegativity of H is 2.05.

**Solution** By Pauling's electronegativity scale

$$\chi_F - \chi_H = 0.182\sqrt{\Delta_{H-F}}$$

(Values of BE are in kcal)

$$\Delta_{H-F} = E_{HF} - \sqrt{E_{H-H} \cdot E_{F-F}}$$

$$= 134.6 - \sqrt{104.2 \times 36.6}$$

$$= 72.84 \text{ kcal}$$

$$\chi_F - \chi_H = 0.182\sqrt{72.84} = 1.5534$$

$$\begin{aligned} \therefore \quad \chi_F &= \chi_H + 1.5534 \\ &= 3.6034 \end{aligned}$$

**Problem 15.**  $(IE)_1$  and  $(IE)_2$  of  $Mg(g)$  are 740 kJ mol<sup>-1</sup>. Calculate percentage of  $Mg^+(g)$  and  $Mg^{2+}(g)$  if 50.0 kJ of energy is absorbed.

**Solution** Number of moles of  $Mg(g) = \frac{1}{24} = 0.0417$

Energy absorbed in the ionisation of  $Mg(g)$

$$= 0.0417 \times 740$$

$$= 30.83 \text{ kJ}$$

$$\text{Energy unused} = 50 - 30.83 = 19.17 \text{ kJ}$$

19.17 kJ will be used in the ionisation of  $Mg^+(g)$

Hence, number of moles of  $Mg^+(g)$  converted to  $Mg^{2+}(g)$

$$= \frac{19.17}{1450} = 0.0132$$

$$Mg^+(g) \text{ left as } Mg^+(g) = 0.0417 - 0.0132 = 0.0285$$

$$\therefore \text{ Percentage of } Mg^+(g) = \frac{0.0285}{0.0417} \times 100 = 68.34\%$$

$$\text{and percentage of } Mg^{2+}(g) = 31.65\%$$



# Master Exercises

## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

1. Comment on the following melting point (given in °C) sequences.

|         |          |
|---------|----------|
| Cu 1083 | Zn 419.5 |
| Ag 961  | Cd 320.8 |
| Au 1064 | Hg -38.9 |

2. For the effective nuclear charge for the last valence electron ( $n$ ) of the second period

$$Z^* = 0.65 + 0.65n = 0.65[1 + n]$$

Calculate  $Z^*$  for Li, Be, B and C.

3. Compute the oxidation numbers of each element in the ions

|                                  |                                 |
|----------------------------------|---------------------------------|
| (a) $\text{H}_2\text{IO}_6^{3-}$ | (b) $\text{S}_3\text{O}_6^{2-}$ |
| (c) $\text{Na}_2\text{O}_2$      |                                 |

4. Rank the 5s, 5p, 5d, 5f and 5g orbitals in order of increasing

- (a) penetrating ability
- (b) shielding ability and
- (c) degree to which they are shielded by inner electrons

5. The single-bonded metallic radius of Na is 157 pm. Give a reasonable estimate of the following radii, assuming that the increment between radii of different magnitudes is 60 pm

- (a) the covalent radius of Na
- (b) the cationic radius of Na
- (c) the anionic radius of Na
- (d) the van der Waals' radius of Na

6. Without the use of tables, arrange each of the following sets in order of increasing size

- |                       |                    |
|-----------------------|--------------------|
| (a) Li, C, F, Ne      | (b) Be, Ca, Ba, Ra |
| (c) B, Al, Ga, In, Tl | (d) V, Nb, Ta, Db  |

7. Fill in each blank with one of the following; increase; decrease; stay the same; more rapidly; less rapidly.

- (a) Electronegativities of atoms ..... from left to right across a period.
- (b) Electronegativities of atoms ..... from top to bottom down a group.

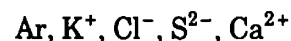
- (c) Electronegativities of atoms change ..... when crossing the *d*-block of elements than when crossing the *p*-block.

- (d) Theoretical radii of atoms  $< r_{\text{max}} >$  ..... from left to right across the *f*-block in the sixth period, but real radii ..... across the *f*-block ..... than they do across the *p*-block.

- (e) Radii of atoms ..... from top to bottom going down group 2; radii ..... from top to bottom going down Group 13(III).

### Analytical Questions

1. Arrange the following species in order of increasing size :



2. Refer to the Periodic Table and identify :

- (a) an element that is both in group 15 (IIIA) and in the fifth period
- (b) an element similar to sulphur
- (c) a highly reactive metal in the sixth period
- (d) the halogen element in the fifth period
- (e) an element with atomic number greater than 50 that is similar to the element with atomic number 18.

3. Match each of the lettered items in the column on the left with an appropriate numbered items in the column on the right. Some of the numbered items may be used more than once, and some not at all.

- |                       |                                                            |
|-----------------------|------------------------------------------------------------|
| (a) Tl                | 1. an alkaline-earth metal                                 |
| (b) $Z = 70$          | 2. element in the fifth period and group 15 (VA)           |
| (c) Ni                | 3. largest atomic radius of all the elements               |
| (d) $[\text{Ar}]4s^2$ | 4. an element in the fourth period and group 16(VIA)       |
| (e) a metalloid       | 5. $3d^8$                                                  |
| (f) a non-metal       | 6. one <i>p</i> -electron in the shell of highest <i>n</i> |
|                       | 7. <i>d</i> -block element                                 |
|                       | 8. <i>f</i> -block element                                 |

4. For each of the following pairs, indicate the atom that has the larger size :

(a) Br or As (b) Sr or Mg  
(c) Ca or Cs (d) Ne or Xe  
(e) C or O (f) Hg or Cl

5. Arrange the following in the increasing value of  $(IE)_1$  :

Sr, Cs, S, F, As

6. Listed below are the electronic configuration of five elements. Arrange the elements in the increasing order of metallic character :

(a)  $[Ar] 3d^{10} 4s^2$  (b)  $[Ar] 4s^2$   
(c)  $[Ar] 3d^{10} 4s^2 4p^6 5s^2$  (d)  $[Ar] 3d^{10} 4s^2 4p^5$   
(e)  $[Ar] 3d^{10} 4s^2 4p^6 5s^1$

7. With reference only to the Periodic Table, indicate which of the atoms Bi, S, Ba, As and Ca :

(a) is most metallic;  
(b) is most non-metallic;  
(c) has the intermediate value when the five are arranged in order of increasing first ionisation energy.

8. Arrange the following elements in order of decreasing metallic character : Sc, Fe, Rb, Br, O, Ca, F, Te.

9. Which of the following species would you expect to be diamagnetic and which paramagnetic :  $K^+$ ,  $Cr^{3+}$ ,  $Zn^{2+}$ ,  $Cd$ ,  $Co^{3+}$ ,  $Sn^{2+}$ , Br.

10. Assuming that the seventh period is 32 members long, what should be the atomic number of the noble gas following radon (Rn)? Of the alkali metal following francium (Fr)? What would you expect their approximate atomic weights to be?

11. Use the following system of naming elements in which first alphabets of the digits are written collectively,

0 1 2 3 4 5 6 7 8 9  
nil uni bi tri quad pent hex sept oct enn

to write three-letter symbol for the elements with atomic number 101 to 109.

[Example : 101 is Unu ...]

12. Match the following lettered items in the column on the left with an appropriate numbered items in the column on the right. All the numbered items should be used at least once, and some must be used more than once :

(a)  $Z = 37$  1. two unpaired  $p$ -electrons  
(b)  $Z = 9$  2. diamagnetic  
(c)  $Z = 16$  3. more negative electron affinity than elements on either side of it in the same period.  
(d)  $Z = 30$  4. lower  $(IE)_1$  than Ca but greater than Cs.  
(e)  $Z = 82$   
(f)  $Z = 12$

13. Listed below are two atomic properties of the element germanium. Refer to the Periodic Table and indicate

probable values for each of the following elements, expressed as greater than, about equal to, or less than the value for Ge.

|        | Covalent radius | $(IE)_1$                 |
|--------|-----------------|--------------------------|
| (a) Ge | 122 pm          | 762 kJ mol <sup>-1</sup> |
| (b) Al |                 |                          |
| (c) In | $> \leq$        | $> \leq$                 |
| (d) Se |                 |                          |

14. For the following groups of elements, select the one that has the property noted

(a) The largest atom : H, Ar, Ag, Ba, Te, Au  
(b) The lowest  $(IE)_1$  : B, Sc, Al, Br, Mg, Pb  
(c) The smallest (most negative)  $(EA)$  : Na, I, Ba, Se, Cl, P  
(d) The largest number of unpaired electrons : F, N,  $S^{2-}$ ,  $Mg^{2+}$ ,  $Sc^{3+}$ ,  $Ti^{3+}$

15. An element is oxidised by fluorine and not by chlorine. Could the element be sodium? Aluminum? Sulphur? Oxygen? Explain your answer.

16. Explain why the most negative oxidation state of an atom of group 15 (VA) element is equal to the number of electrons required to fill the valence shell of the neutral atom?

17. Predict which member of each of the following pairs will

(a) conduct electricity : Ca or S?  
(b) form a negative ion : Co or Cl?  
(c) form a solution of an acid in water :  $N_2O_3$  or CaO?  
(d) form an ionic compound with fluorine : Al or P?  
(e) form a covalent compound with O : K or N?  
(f) have a higher electronegativity : Ba or Br  
(g) form a solution of base in water :  $CO_2$  or BaO  
(h) a base : CsOH or BrOH  
(i) an acid :  $In(OH)_3$  or  $B(OH)_3$   
(j) an oxidising agent : S or Na  
(k) an ionic compound : RbCl or BrCl  
(l) more easily reduced : Ca or O  
(m) react as a base :  $P(OH)_3$  or  $Al(OH)_3$   
(n) contain ions :  $KNO_2$  or  $ClNO_2$   
(o) easily hydrated :  $Li^+$  or  $Na^+$   
(p) greater  $(IE)_1$  : Be or B  
(q) greater  $(EA)$  : F or  $Cl^-$   
(r) positive  $(EA)$  : F or  $O^-$   
(s) greater  $(IE)_2$  : N or O

- (t) max.  $(IE)_1$  :  $Na^+, Ne^+, F^+, O^+$   
 (u) zero  $(EN)$  : Ne or Na  
 (v) liquid element : Hg or Zn  
 (w) amphoteric oxide :  $B_2O_3, Al_2O_3$   
 (x) acidic oxide :  $B_2O_3, Al_2O_3$   
 (y) basic oxide :  $N_2O_5, In_2O_3$   
 (z) harder element : carbon (diamond) or lead

18. Match each of the following elements on the right with its description on the left :

- (a) A dark-red liquid I : Ca  
 (b) A colourless gas that burns in oxygen gas II : Au  
 (c) A reactive metal that attacks water III :  $H_2$   
 (d) A totally inert gas IV : Ar  
 (e) A shiny metal that is used in jewellery V :  $Br_2$

19. You are given four substances: a fuming red liquid, a dark metallic-looking solid, a pale yellow gas, and a yellow-green gas that attacks glass. You are told that these substances are the first four members of group VIIA. Name each.

20. A student is given samples of three elements, X, Y, and Z, which could be an alkali metal, a member of group IVA, and a member of group VA. She makes the following observations :

Element X has a metallic lusture and conducts electricity. It reacts slowly with aq HCl to produce

$H_2$  gas. Element Y is a light-yellow solid and does not conduct electricity. Element Z has a metallic lusture and conducts electricity. When exposed to air, it slowly forms a white powder aqueous solution of which is basic. What can you conclude about the elements from these observations?

21. Listed below are the locations of certain elements in groups and periods of the Periodic Table. Arrange these elements in the expected order of increasing first ionisation energy.

- (a) element in the fourth period and group IVA  
 (b) element in the third period and group VIA  
 (c) element in the sixth period and group IIIA  
 (d) element in the second period and group VIIIA  
 (e) element in the fourth period and group VIA

22. The  $(IE)_1$  and the  $(IE)_2$  (in  $kJ\ mol^{-1}$ ), of three elements I, II and III are given below :

|          | I    | II   | III  |
|----------|------|------|------|
| $(IE)_1$ | 403  | 549  | 1142 |
| $(IE)_2$ | 2640 | 1060 | 2080 |

Identify the element which is likely to be :

- (a) a non-metal  
 (b) an alkali metal  
 (c) an alkaline-earth metal

23. The element 119 has not been discovered. What would be the IUPAC name and the symbol for this element? Write the formula of the most stable chloride and oxide.

## Exercise 2

### (Stage 2 : High Skill Problem Solving)

#### Only One Option Correct

1. If Aufbau rule is not followed, K-19 will be placed in ..... block.

- (a) s (b) p  
 (c) d (d) f

2. First, second and third IP values are 100 eV, 150 eV and 1500 eV. Element can be

- (a) Be (b) B  
 (c) F (d) Na

3. Which has maximum ionisation potential?

- (a) N (b) O  
 (c)  $O^+$  (d) Na

4.  $N_0/2$  atoms of  $X(g)$  are converted into  $X^+(g)$  by energy  $E_1$ .  $N_0/2$  atoms of  $X(g)$  are converted into  $X^-(g)$  by energy  $E_2$ . Hence, ionisation potential and electron affinity of  $X(g)$  are

- (a)  $\frac{2E_1}{N_0}, \frac{2(E_1 - E_2)}{N_0}$  (b)  $\frac{2E_1}{N_0}, \frac{2E_2}{N_0}$   
 (c)  $\frac{(E_1 - E_2)}{N_0}, \frac{2E_2}{N_0}$  (d) none is correct

5. Which is maximum hydrated?

- (a) NaCl (b)  $MgCl_2$   
 (c)  $AlCl_3$  (d)  $SiCl_4$

6. Which has maximum polarising power in cation ?

- (a)  $Li^+$  (b)  $Mg^{2+}$   
 (c)  $Al^{3+}$  (d)  $O^{2-}$

7. Electron affinity is positive when

- (a)  $O^-$  is formed from O  
 (b)  $O^{2-}$  is formed from  $O^-$   
 (c)  $O^+$  is formed from O  
 (d) electron affinity is always a negative value

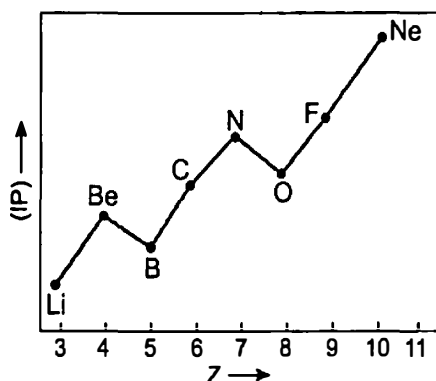
8. Following triads have approximately equal size  
 (a)  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$  (*iso-electronic*)  
 (b)  $\text{F}^-$ ,  $\text{Ne}$ ,  $\text{O}^{2-}$  (*iso-electronic*)  
 (c)  $\text{Fe}$ ,  $\text{Co}$ ,  $\text{Ni}$   
 (d)  $\text{Mn}^+$ ,  $\text{Fe}^{2+}$ ,  $\text{Cr}$  (*iso-electronic*)
9. Ionic radii of  
 (a)  $\text{Ti}^{4+} < \text{Mn}^{7+}$  (b)  $^{35}\text{Cl}^- < ^{37}\text{Cl}^-$   
 (c)  $\text{K}^+ > \text{Cl}^-$  (d)  $\text{P}^{3+} > \text{P}^{5+}$
10. Which of the following ions has the smallest radius?  
 (a)  $\text{Ti}^{2+}$  (b)  $\text{Pt}^{2+}$   
 (c)  $\text{Ni}^{2+}$  (d)  $\text{Zr}^{2+}$
11. When the following five anions are arranged in order of decreasing ionic radius, the correct sequence is  
 (a)  $\text{Se}^{2-}$ ,  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{O}^{2-}$ ,  $\text{F}^-$  (b)  $\text{I}^-$ ,  $\text{Se}^{2-}$ ,  $\text{O}^{2-}$ ,  $\text{Br}^-$ ,  $\text{F}^-$   
 (c)  $\text{Se}^{2-}$ ,  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{F}^-$ ,  $\text{O}^{2-}$  (d)  $\text{I}^-$ ,  $\text{Se}^{2-}$ ,  $\text{Br}^-$ ,  $\text{O}^{2-}$ ,  $\text{F}^-$
12. For which of the following crystals would you expect the assumption of anion-anion contact to be valid?  
 (a)  $\text{CsBr}$  (b)  $\text{NaF}$   
 (c)  $\text{KCl}$  (d)  $\text{NaI}$
13. Which of the following ions has the largest heat of hydration?  
 (a)  $\text{Na}^+$  (b)  $\text{Al}^{3+}$   
 (c)  $\text{F}^-$  (d)  $\text{Sr}^{2+}$
14. Which of the following anions is most easily polarized?  
 (a)  $\text{Cl}^-$  (b)  $\text{Se}^{2-}$   
 (c)  $\text{Br}^-$  (d)  $\text{Te}^{2-}$
15. Of the four  $\Delta H$  values needed to calculate a lattice energy using the Born-Haber cycle, the one that is most difficult to measure is  
 (a) the heat of sublimation of the metal  
 (b) the heat of formation of gaseous atoms of the non-metal  
 (c) the ionization energy of the metal  
 (d) the electron affinity of the non-metal
16. A molecule  $\text{H}-\text{X}$  will be 50% ionic if electronegativity difference of H and X is  
 (a) 1.2 eV (b) 1.4 eV  
 (c) 1.5 eV (d) 1.7 eV
17. Which pair is different from the others?  
 (a)  $\text{Li}-\text{Mg}$  (b)  $\text{Na}-\text{K}$   
 (c)  $\text{Ca}-\text{Mg}$  (d)  $\text{B}-\text{Al}$
18. Which pair is different from the others?  
 (a)  $\text{Li}-\text{Mg}$  (b)  $\text{B}-\text{Si}$   
 (c)  $\text{Be}-\text{Al}$  (d)  $\text{Li}-\text{Na}$
19. Representative elements belong to  
 (a) *s*- and *p*-block (b) *d*-block  
 (c) *d*- and *f*-block (d) *f*-block
20. Covalency is favoured in the following cases  
 (a) a smaller cation  
 (b) a larger anion  
 (c) large charges on cation or anion  
 (d) in all the above cases
21. Inert pair effect is shown by  
 (a) *s*-block (b) *p*-block  
 (c) *d*-block (d) *f*-block
22. Stability of ions of Ge, Sn and Pb will be in the order  
 (a)  $\text{Ge}^{2+} < \text{Sn}^{2+} < \text{Pb}^{2+}$  (b)  $\text{Ge}^{4+} > \text{Sn}^{4+} > \text{Pb}^{4+}$   
 (c)  $\text{Sn}^{4+} > \text{Sn}^{2+}$  (d) all are correct
23. Which is incorrect statement?  
 (a)  $\text{TI}^{3+}$  salts are better oxidising agents  
 (b)  $\text{Ga}^+$  salts are better reducing agents  
 (c)  $\text{Pb}^{4+}$  salts are better oxidising agents  
 (d)  $\text{As}^{5+}$  salts are better oxidising agents
24. The first element of a group in many ways differs from the other heavier members of the group. This is due to  
 (a) the small size  
 (b) the high electronegativity and high ionisation potential  
 (c) the unavailability of *d*-orbitals  
 (d) all of the above
25. Catenation properties of C, Si, Ge, Sn, Pb are in order  
 (a)  $\text{C} \gg \text{Si} > \text{Ge} \approx \text{Sn} \gg \text{Pb}$   
 (b)  $\text{C} < \text{Si} < \text{Ge} < \text{Sn} < \text{Pb}$   
 (c)  $\text{C} > \text{Si} > \text{Sn} > \text{Ge} > \text{Pb}$   
 (d) None of the above is correct
26. Melting points of  $\text{NaCl}$ ,  $\text{NaBr}$ ,  $\text{NaI}$  and  $\text{NaF}$  will be in order  
 (a)  $\text{NaI} < \text{NaBr} < \text{NaCl} < \text{NaF}$   
 (b)  $\text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI}$   
 (c)  $\text{NaBr} < \text{NaF} < \text{NaCl} < \text{NaI}$   
 (d)  $\text{NaCl} < \text{NaI} < \text{NaF} < \text{NaBr}$
27. Melting point is maximum for  
 (a)  $\text{LiCl}$  (b)  $\text{NaCl}$   
 (c)  $\text{KCl}$  (d)  $\text{RbCl}$
28. Which is/are amphoteric oxides?  
 (a)  $\text{BeO}$  (b)  $\text{SnO}$   
 (c)  $\text{ZnO}$  (d) All of these
29. The correct order of increasing ionic character is  
 (a)  $\text{BeCl}_2 < \text{MgCl}_2 < \text{CaCl}_2 < \text{BaCl}_2$   
 (b)  $\text{BeCl}_2 < \text{CaCl}_2 < \text{MgCl}_2 < \text{BaCl}_2$   
 (c)  $\text{BaCl}_2 < \text{CaCl}_2 < \text{MgCl}_2 < \text{BeCl}_2$   
 (d)  $\text{MgCl}_2 < \text{CaCl}_2 < \text{BeCl}_2 < \text{BaCl}_2$
30. Atomic number 64 will have electronic configuration  
 (a)  $[\text{Xe}]_{64} 6s^2 4f^8$  (b)  $[\text{Xe}]_{64} 6s^2 4f^7 5d^1$   
 (c)  $[\text{Xe}]_{64} 4f^{10}$  (d)  $[\text{Xe}]_{64} 6s^2 4f^7 5p^1$
31.  $^{238}_{92}\text{U}$  (IIIB) changes to  $^{234}_{90}\text{Th}$  by emission of  $\alpha$ -particle. Daughter element will be in  
 (a) III B (b) I B  
 (c) V B (d) II A
32. Which is correct order of size of  $\text{O}^-$ ,  $\text{O}^{2-}$ ,  $\text{F}^-$  and  $\text{F}$ ?  
 (a)  $\text{O}^{2-} > \text{O}^- > \text{F}^- > \text{F}$  (b)  $\text{O}^- > \text{O}^{2-} > \text{F}^- > \text{F}$   
 (c)  $\text{O}^{2-} > \text{F}^- > \text{F} > \text{O}^-$  (d)  $\text{O}^{2-} > \text{F}^- > \text{O}^- > \text{F}$

33. The electronegativities of N, C, Si and P are such that  
 (a)  $P < Si < C < N$  (b)  $Si < P < N < C$   
 (c)  $Si < P < C < N$  (d)  $P < Si < N < C$
34. The electron affinities of N, O, S and Cl are such that  
 (a)  $N < O < S < Cl$  (b)  $O < N < Cl < S$   
 (c)  $O \approx Cl < N \approx S$  (d)  $O < S < Cl < N$
35. Fluorine has the highest electronegativity among the  $ns^2 np^5$  group on the Pauling scale, but the electron affinity of fluorine is less than that of chlorine because  
 (a) the atomic number of fluorine is less than that of chlorine  
 (b) fluorine being the first member of the family behaves in an unusual manner  
 (c) chlorine can accommodate an electron better than fluorine by utilising its vacant  $3d$ -orbital  
 (d) small size, high electron density and an increased electron repulsion makes addition of an electron to fluorine less favourable than that in the case of chlorine.
36. (A), (B), (C) are elements in the third short period. Oxide of (A) is ionic, that of (B) is amphoteric and of (C) a giant molecule. (A), (B) and (C) will have atomic number in the order  
 (a)  $(A) < (B) < (C)$  (b)  $(C) < (B) < (A)$   
 (c)  $(A) < (C) < (B)$  (d)  $(B) < (A) < (C)$
37. Going down in a group from F to I, which of the following properties decreases?  
 (a) Ionic radius (b) Ionisation energy  
 (c) Oxidising power (d) Electronegativity
38. Which of the following will have maximum electron affinity?  
 (a)  $1s^2 2s^2 2p^5$  (b)  $1s^2 2s^2 2p^6$   
 (c)  $1s^2 2s^2 2p^6 3s^2 3p^5$  (d)  $1s^2 2s^2 2p^6 3s^2 3p^6$
39. Size of cation is smaller than that of the atom because of  
 (a) the whole of the outer shell of electrons is removed  
 (b) effective nuclear charge increases  
 (c) due to gain of electrons  
 (d) statement, that cation is smaller than atom, is wrong
40. The sizes of the second and third row transition elements being almost the same. This is due to  
 (a)  $d$ - and  $f$ -orbitals do not shield the nuclear charge very effectively  
 (b) lanthanide contraction  
 (c) both (a) and (b) are true  
 (d) None of the above is true
41. The factors that influence the ionisation energies are  
 (a) the size of the atom  
 (b) the charge on the nucleus  
 (c) how effectively the inner electron shell screen the nuclear charge  
 (d) all of the above
42. Following are the values of the electron affinities (in  $\text{kJ mol}^{-1}$ ) the formation of  $O^-$  and  $O^{2-}$  from O  
 (a)  $-142, -702$  (b)  $-142, 702$   
 (c)  $142, 702$  (d)  $-142, -142$
43. The ionic radii of  $O^{2-}$ ,  $F^-$ ,  $Na^+$  and  $Mg^{2+}$  are 1.35, 1.34, 0.95 and 0.66 Å respectively. The radius of the Ne atom is  
 (a) 1.39 Å (b) 1.12 Å  
 (c) 0.85 Å (d) 0.50 Å
44. The element which does not exist in liquid state at room temperature are  
 (a) Na (b) Br  
 (c) Hg (d) Ga
45. The statement that is not correct for the periodic classification of elements is  
 (a) the properties of elements are the periodic functions of their atomic numbers  
 (b) non-metallic elements are lesser in number than metallic elements  
 (c) the first ionisation energies of elements along a period do not vary in a regular manner with increase in atomic number  
 (d) for transition elements the  $d$ -subshells are filled with electrons monotonically with increase in atomic number
46. Which one of the following has the maximum number of unpaired electrons?  
 (a)  $Mg^{2+}$  (b)  $Ti^{3+}$   
 (c)  $V^{3+}$  (d)  $Fe^{2+}$
47. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order  
 $ClOH$  (I)  $BrOH$  (II)  $IOH$  (III)  
 (a)  $I > II > III$  (b)  $II > I > III$   
 (c)  $III > II > I$  (d)  $I > III > II$
48. The statement is not true for the long form of the Periodic Table  
 (a) It reflects the sequence of filling the electrons in the order of the sub-energy shells  $s$ ,  $p$ ,  $d$  and  $f$   
 (b) It helps to predict the stable valency states of the elements  
 (c) It reflects trends in physical and chemical properties of the elements  
 (d) It helps to predict the relative ionicity of the bond between any two elements
49. The electronic configuration  $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2$  is for  
 (a)  $f$ -block element (b)  $d$ -block element  
 (c)  $p$ -block element (d)  $s$ -block element
50. Which of the following statement is false?  
 (a) Elements of IB and IIB groups are transition elements  
 (b) Elements of VB group do not contain metalloids

- (c) Elements of IA and IIA groups are normal elements  
 (d) Elements of IVB group are neither strongly electronegative nor strongly electropositive.

51. Transition metals are characterised by the properties  
 (a) variable valency and tendency to form complex  
 (b) coloured compounds  
 (c) high melting and boiling points  
 (d) all of the above

52. Following graph shows variation of ionisation potential (IP) with atomic number in second period (Li—Ne). Value of ionisation potential (IP) of Na (11) will be



- (a) above Ne  
 (b) below Ne but above O  
 (c) below Li  
 (d) between N and O

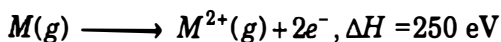
53. Based on the fig. in Q. 52, which is incorrect statement

- (a)  $I_1$  of Be  $> I_1$  of B but  $I_2$  of Be  $< I_2$  of B  
 (b)  $I_1$  of Be  $< I_1$  of B but  $I_2$  of Be  $< I_2$  of B  
 (c)  $I_2$  of Be  $< I_1$  of B<sup>+</sup>  
 (d)  $I_1$  of Be<sup>2+</sup> is abnormally high

54. Which is/are correct order of ionic mobility?

- (a) Li<sup>+</sup>  $<$  Na<sup>+</sup>  $<$  K<sup>+</sup>  
 (b) Al<sup>3+</sup>  $<$  Mg<sup>2+</sup>  $<$  Na<sup>+</sup>  
 (c) Both (a) and (b)  
 (d) None of these

55.  $M(g) \longrightarrow M^+(g) + e^-$ ,  $\Delta H = 100$  eV



which is incorrect statement?

- (a)  $I_1$  of  $M(g)$  is 100 eV  
 (b)  $I_1$  of  $M^+(g)$  is 150 eV  
 (c)  $I_2$  of  $M(g)$  is 250 eV  
 (d)  $I_2$  of  $M(g)$  is 150 eV

56. AB is predominantly ionic as  $A^+B^-$  if

- (a)  $(IP)_A < (IP)_B$   
 (b)  $(EA)_A < (EA)_B$   
 (c)  $(EN)_A < (EN)_B$   
 (d)  $(IP)_B < (IP)_A$

(IP stands for ionisation potential, EA for electron affinity and EN for electronegativity).

57. EN of the element (A) is  $E_1$  and IP is  $E_2$ . Hence, EA will be

- (a)  $2E_1 - E_2$   
 (b)  $E_1 - E_2$   
 (c)  $E_1 - 2E_2$   
 (d)  $(E_1 + E_2)/2$

58. Stability order of group IIIA (boron family) element is

- (a) Ga<sup>+</sup>  $<$  In<sup>+</sup>  $<$  Tl<sup>+</sup>  
 (b) Ga<sup>3+</sup>  $>$  Ga<sup>+</sup>  
 (c) both (a) & (b)  
 (d) None of these

59. The metal which gives no amphoteric oxide is

- (a) Zn  
 (b) Cu  
 (c) Sn  
 (d) Al

60. The first ionisation potential (in eV) of N, O atoms are

- (a) 14.6, 13.6  
 (b) 13.6, 14.6  
 (c) 13.6, 13.6  
 (d) 14.6, 14.6

61. Atomic radii of F and Ne in Å are given by

- (a) 0.72, 1.6  
 (b) 1.6, 1.6  
 (c) 0.72, 0.72  
 (d) none of these

62. Match list-I (atomic number of elements) with list-II (position of elements in Periodic Table) and select the correct answer using the codes given below the lists

#### List I

- A. 19  
 B. 22  
 C. 32  
 D. 64

#### List II

1. p-block  
 2. f-block  
 3. d-block  
 4. s-block

#### Codes

- |     | A | B | C | D |
|-----|---|---|---|---|
| (a) | 1 | 2 | 3 | 4 |
| (b) | 4 | 3 | 1 | 2 |
| (c) | 4 | 1 | 3 | 2 |
| (d) | 2 | 1 | 3 | 4 |

63. Fluorine does not form any polyhalide as other halogens because

- (a) it has maximum ionic character  
 (b) it has low F—F bond energy (38.5 kcal mol<sup>-1</sup>)  
 (c) of the absence of d-orbitals in the valence shell of fluorine  
 (d) it brings about maximum coordination number in other elements

64. Consider the following statements

1. Cs<sup>+</sup> is more highly hydrated than the other alkali metal ions.
2. Among the alkali metals Li, Na, K and Rb, lithium has the highest melting point.
3. Among the alkali metals only lithium forms a stable nitride by direct combination.

Of these statements

- (a) 1, 2 and 3 are correct  
 (b) 1 and 2 are correct  
 (c) 1 and 3 are correct  
 (d) 2 and 3 are correct

65. Match list I (atomic number of the elements) with list II (position in the Periodic Table) and select the correct answer using the codes given below the lists:

#### List I

- A. 52  
 B. 56  
 C. 57  
 D. 60

#### List II

1. s-block  
 2. p-block  
 3. d-block  
 4. f-block

## Codes

|     | A | B | C | D |
|-----|---|---|---|---|
| (a) | 2 | 1 | 3 | 4 |
| (c) | 1 | 2 | 3 | 4 |

|     | A | B | C | D |
|-----|---|---|---|---|
| (b) | 2 | 1 | 4 | 3 |
| (d) | 1 | 2 | 4 | 3 |

66. If Aufbau and Hund's rule are not used, then incorrect statement is

- (a)  $K^+$  would be coloured ion  
 (b) Na will be in same  $s$ -block (if these rules are true)  
 (c) Cu would be  $s$ -block element  
 (d) magnetic moment of Cr(24) would be zero

67. Which set has all the coloured ions?

- (a)  $Cu^+$ ,  $Cu^{2+}$ ,  $Ni^{2+}$  (b)  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$   
 (c)  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Sc^{3+}$  (d)  $Na^+$ ,  $Mg^{2+}$ ,  $Al^{3+}$

68. For the element (X), student (A) measured its radius as 102 nm, student (B) as 103 nm and (C) as 100 nm using same apparatus. Their teacher explained that measurements were correct by saying that recorded values by (A), (B) and (C) are

- (a) crystal, van der Waals' and covalent radii  
 (b) covalent, crystal and van der Waals' radii  
 (c) van der Waals', ionic and covalent  
 (d) none of the above is correct

69. Which set shows inert pair effect?

- (a) Fe, Co, Ni (b) B, Al, Ga  
 (c) Ge, Sn, Pb (d) He, Ne, Ar

70. Gd (64) has ..... unpaired electrons with sum of spin .....

- (a) 7, 3.5 (b) 8, 3  
 (c) 6, 3 (d) 8, 4

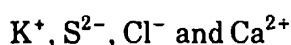
71. Element Unq has atomic number of

- (a) 102 (b) 103  
 (c) 104 (d) 112

72. The relative thermal stabilities of alkali metal halides are such that

- (a)  $CsCl > RbCl > KCl > NaCl > LiCl$   
 (b)  $LiCl > NaCl > KCl > RbCl > CsCl$   
 (c)  $CsCl > RbCl < KCl > NaCl < LiCl$   
 (d)  $CsCl < RbCl > KCl < NaCl > LiCl$

73. Consider the isoelectronic ions



The radii of these ionic species follow the order

- (a)  $Ca^{2+} > K^+ > Cl^- > S^{2-}$  (b)  $Cl^- > S^{2-} > K^+ > Ca^{2+}$   
 (c)  $S^{2-} > Cl^- > K^+ > Ca^{2+}$  (d)  $K^+ > Ca^{2+} > S^{2-} > Cl^-$

74. Astatine is the last element in halogen group (VII). It is expected to be

- (a) more electronegative than iodine  
 (b) composed of diatomic molecules  
 (c) limited to an oxidation number of  $-1$  in its compounds  
 (d) a solid at room temperature

75. The first ionisation potential of Al is smaller than that of Mg because

- (a) the atomic size of Al  $>$  Mg  
 (b) the atomic size of Al  $<$  Mg  
 (c) Al has one unpaired electron in  $p$ -orbital  
 (d) the atomic number of Al  $>$  Mg

76. The non-metallic cation is in

- (a)  $CrO_2Cl_2$  (b)  $VOCl$   
 (c)  $NH_4Cl$  (d)  $PCl_3$

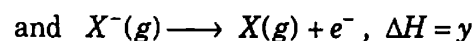
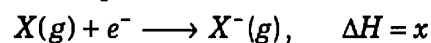
77. Which of the following properties shows a clear periodic variation?

- (a) First ionisation energy  
 (b) Molar mass of the element  
 (c) Number of isotopes of the atom  
 (d) All of the above

78. Ionisation energy of the element  $X(g)$  is  $I$  and the electron affinity of  $X^+(g)$  is  $E$  then

- (a)  $I = E$  (b)  $I = -E$   
 (c)  $I = \frac{E}{2}$  (d)  $I = -\frac{E}{2}$

79. For the process



Select correct alternate

- (a) Ionisation energy of  $X^-(g)$  is  $y$   
 (b) Electron affinity of  $X(g)$  is  $x$   
 (c) Electron affinity of  $X(g)$  is  $-y$   
 (d) All the above are correct statements

80. The most metallic of the following elements is

- (a) Mg (b) Li  
 (c) K (d) Ca

81. The most negative electron affinity of the following elements is that of

- (a) Br (b) Sn  
 (c) Ba (d) Li

82. The highest first ionisation energy of the following elements is that of

- (a) Cs (b) Cl  
 (c) I (d) Li

83. The heat of hydration of  $Ca^{2+}$ ,  $Sr^{2+}$  and  $Ba^{2+}$  in the decreasing order is

- (a)  $Ca^{2+} > Sr^{2+} > Ba^{2+}$  (b)  $Ca^{2+} > Ba^{2+} > Sr^{2+}$   
 (c)  $Sr^{2+} > Ba^{2+} > Ca^{2+}$  (d)  $Ba^{2+} > Sr^{2+} > Ca^{2+}$

84. The compound of vanadium has magnetic moment of 1.73 BM. The vanadium chloride has the formula

- (a)  $VCl_2$  (b)  $VCl_3$   
 (c)  $VCl_4$  (d)  $VCl_5$

85. Which of the following does not represent the correct order of the properties indicated?  
 (a)  $\text{Ni}^{2+} > \text{Cr}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+}$  (size)  
 (b)  $\text{Sc} > \text{Ti} > \text{Cr} > \text{Mn}$  (size)  
 (c)  $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+}$  (unpaired electron)  
 (d)  $\text{Fe}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+}$  (unpaired electron)
86. Which of the following order is wrong?  
 (a)  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3$  — acidic  
 (b)  $\text{Li} < \text{Be} < \text{B} < \text{C}$  —  $(\text{IE})_1$   
 (c)  $\text{Al}_2\text{O}_3 < \text{MgO} < \text{Na}_2\text{O} < \text{K}_2\text{O}$  — basic  
 (d)  $\text{Li}^{2+} < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$  — ionic radius
87. The ions  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  are isoelectronic. Their ionic radii show  
 (a) an increase from  $\text{O}^{2-}$  to  $\text{F}^-$  and then decrease from  $\text{Na}^+$  to  $\text{Al}^{3+}$   
 (b) a decrease from  $\text{O}^{2-}$  to  $\text{F}^-$  and then increase from  $\text{Na}^+$  to  $\text{Al}^{3+}$   
 (c) a significant increase from  $\text{O}^{2-}$  to  $\text{Al}^{3+}$   
 (d) a significant decrease from  $\text{O}^{2-}$  to  $\text{Al}^{3+}$
88. Ionic radii are  
 (a) inversely proportional to effective nuclear charge  
 (b) inversely proportional to square of effective nuclear charge  
 (c) directly proportional to effective nuclear charge  
 (d) directly proportional to square of effective nuclear charge
89. Sodium forms  $\text{Na}^+$  ion but it does not form  $\text{Na}^{2+}$  because  
 (a) very low value of  $(\text{IE})_1$  and  $(\text{IE})_2$   
 (b) very high value of  $(\text{IE})_1$  and  $(\text{IE})_2$   
 (c) low value of  $(\text{IE})_1$  and low value of  $(\text{IE})_2$   
 (d) low value of  $(\text{IE})_1$  and high value of  $(\text{IE})_2$
90. The correct decreasing order of ionic radius is  
 (a)  $\text{C}^{4-} > \text{N}^{3-} > \text{O}^{2-} > \text{F}^-$  (b)  $\text{F}^- > \text{O}^{2-} > \text{N}^{3-} > \text{C}^{4-}$   
 (c)  $\text{O}^{2-} > \text{F}^- > \text{C}^{4-} > \text{N}^{3-}$  (d)  $\text{N}^{3-} > \text{O}^{2-} > \text{F}^- > \text{C}^{4-}$
91. First long period contains ..... elements.  
 (a) 8 (b) 18  
 (c) 32 (d) 2
92. Recently (in 2003) element with atomic number 110 has been named by IUPAC as  
 (a) Hs (b) Mt  
 (c) Ds (d) Sg
93. Recently (in Aug 2003) two new elements have been discovered with atomic numbers  
 (a) 113, 114 (b) 114, 115  
 (c) 115, 116 (d) 113, 115
94. Element 113 is produced via  
 (a)  $\alpha$ -decay of element 115  
 (b)  $\beta$ -decay of element 114  
 (c)  $\alpha$ -decay of element 111  
 (d)  $\beta$ -decay of element 112
95. Numbering of groups as 1, 2, ..... 18 was adopted by IUPAC in  
 (a) 1986 (b) 1906  
 (c) 1908 (d) 1988
96. Element with valence shell-electronic configuration as  $(n-1)d^5 ns^1$  is placed in  
 (a) IA, s-block (b) VIA, s-block  
 (c) VIB, s-block (d) VIB, d-block
97. Which set does not show correct matching?  
 (a)  $\text{Sc}^{3+} [\text{Ne}] 3s^2 3p^6$  zero group  
 (b)  $\text{Fe}^{2+} [\text{Ar}] 3d^6$  VIII group  
 (c)  $\text{Cr} [\text{Ar}] 3d^5 4s^1$  VIB group  
 (d) All of the above
98. Two new elements (discovered in Aug 2003) with atomic number 113 and 115 are to be placed in  
 (a) s-block (b) p-block  
 (c) d-block (d) f-block
99. Most stable cation of element 113 will be  
 (a)  $M^{3+}$  (b)  $M^{2+}$   
 (c)  $M^+$  (d)  $M_2^{2+}$
100. Element with atomic number 115 has configuration as ..... and with most stable cation as .....  
 (a)  $[\text{Rn}] 7s^2 5d^{10} 4f^{14} 7p^3$   $M^{3+}$   
 (b)  $[\text{Rn}] 7s^2 5d^{10} 4f^{14} 7p^3$   $M^{5+}$   
 (c)  $[\text{Rn}] 7s^2 5d^{10} 4f^{14} 7p^3$   $M^+$   
 (d)  $[\text{Rn}] 5d^{10} 4f^{14} 7p^5$   $M^{5+}$
101. Main group elements constitute:  
 (a) s-and p-block (b) p-and d-block  
 (c) s-and d-block (d) d-and f-block
102. Elements X and Y have valence shell electron configuration as  
 $X: ns^2 np^5$ ;  $Y: ns^1$   
 Which compound is likely formed from X and Y?  
 (a)  $X_3Y_5$  (b)  $Y_3X_5$   
 (c) XY (d) YX
103. Recently discovered elements (August 2003) with atomic number 113 and 115 have valence electrons in  
 (a) s-orbital (b) p-orbital  
 (c) d-orbital (d) f-orbital
104. Chalcogens are elements of  
 (a) group 16 (b) p-block  
 (c)  $ns^2 np^4$  configuration (d) all are correct
105.  $M^{3+}$  has electronic configuration as  $[\text{Ar}] 3d^{10}$ , hence it lies in  
 (a) s-block (b) p-block  
 (c) d-block (d) f-block
106. Transition elements have vacant  
 (a) s-orbitals (b) p-orbitals  
 (c) d-orbitals (d) f-orbitals
107. Of the following pairs, the one containing examples of metalloid elements in the Periodic Table is  
 (a) Na and K (b) F and Cl  
 (c) Cu and Ag (d) B and Si
108. Pick out the property which is not shown by transition elements.



- (a) Show variable oxidation state  
(b) Impart colour to flame  
(c) Are paramagnetic in nature  
(d) Act as catalytic agents
109. Which of the following is a transition element?  
(a) Al (b) As  
(c) Ni (d) Rb
110. Which of the following has the electronic configuration  $[\text{Ar}] 3d^5$ ?  
(a) Cr (b)  $\text{Fe}^{3+}$   
(c) Mn (d) V
111. Which of the following forms a stable +4 oxidation state?  
(a) Lanthanum (b) Cerium  
(c) Europium (d) Gadolinium
112. The lanthanides have electron configuration with  $6s^2$  in common but with variable occupation of the  
(a)  $6p$ -level (b)  $5p$ -level  
(c)  $5d$ -level (d)  $4f$ -level
113. Which group of elements is analogous to the lanthanides?  
(a) Halides (b) Actinides  
(c) Chalcogenides (d) Borides
114. EC of Gd (64) is written as  
(a)  $[\text{Xe}]_{64} 4f^7 5d^1 6s^2$  (b)  $[\text{Xe}]_{64} 4f^8 6s^2$   
(c)  $[\text{Xe}]_{64} 4f^9 6s^1$  (d)  $[\text{Xe}]_{64} 4f^{10}$
115. Recently discovered element with atomic number 115 is  
(a) Uun (b) Uub  
(c) Uup (d) Uus
116. In Periodic Table, metallic elements appear  
(a) in the left-hand columns  
(b) in the top rows  
(c) in the right-hand columns  
(d) in the bottom rows
117. The atoms of the elements belonging to the same group of the Periodic Table will have  
(a) the same number of protons  
(b) the same number of electrons in the valence-shell  
(c) the same number of neutrons  
(d) the same number of electrons
118. Which will have graded property similar to EC  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ ?  
(a)  $[\text{Ar}] 3d^{10} 4s^1$  (b)  $[\text{Kr}] 4d^{10} 5s^1$   
(c)  $[\text{Kr}] 5s^1$  (d) All of these
119. Recently discovered element with atomic number 115 has configuration  
(a)  $ns^2 np^3$  (b)  $ns^2 np^1$   
(c)  $ns^2 np^5$  (d)  $ns^2 np^2$
120. Element with atomic number 113 has been reported in August 2003. Its electronic configuration is similar to that of  
(a) Si (b) Ga  
(c) Bi (d) At
121. Which has maximum stability?  
(a)  $\text{AsCl}_3$  (b)  $\text{SbCl}_3$   
(c)  $\text{BiCl}_3$  (d) Equal
122. Which reaction is most spontaneous?  
(a)  $\text{Ga}^{3+} + 2e^- \longrightarrow \text{Ga}^+$  (b)  $\text{In}^{3+} + 2e^- \longrightarrow \text{In}^+$   
(c)  $\text{Tl}^{3+} + 2e^- \longrightarrow \text{Tl}^+$  (d) Cannot be predicted
123. With respect to oxygen maximum valency is shown by  
(a) halogen family (b) oxygen family  
(c) nitrogen family (d) boron family
124. Which is best oxidising agent?  
(a)  $\text{Ge}^{4+}$  (b)  $\text{Pb}^{4+}$   
(c)  $\text{Sn}^{4+}$  (d)  $\text{Sn}^{2+}$
125. Valence electrons in the element A are 3 and that in element B are 6. Most probable compound formed from A and B is  
(a)  $\text{A}_2\text{B}$  (b)  $\text{AB}_2$   
(c)  $\text{A}_6\text{B}_3$  (d)  $\text{A}_2\text{B}_3$
126. The relative extent to which the various orbitals penetrate the electron clouds of other orbitals is  
(a)  $s > p > d > f$  (b)  $s < p < d < f$   
(c)  $s < d < p < f$  (d)  $d < s < p < f$
127. Screening effect is not observed in  
(a)  $\text{He}^+$  (b)  $\text{Li}^{2+}$   
(c)  $\text{Be}^{3+}$  (d) in all cases
128. In which case effective nuclear charge is minimum?  
(a) Be (b)  $\text{Be}^{2+}$   
(c)  $\text{Be}^{3+}$  (d) Equal
129. For Be,  $Z_{\text{eff}} = 1.95$  and for  $\text{Be}^{x+}$ ,  $Z_{\text{eff}} = 2.30$ . Hence, ion is  
(a)  $\text{Be}^+$  (b)  $\text{Be}^{2+}$   
(c)  $\text{Be}^{3+}$  (d)  $\text{Be}^0$
130. For Cu, effective nuclear charge felt by a  $4s$ -electron is  
(a) 2.2 (b) 2.95  
(c) 1.0 (d) 1.65
131. State, which one of the following has the largest atomic radius?  
(a) Cs (b) Mg  
(c) Ba (d) Cr
132. Which one of the following has the smallest atomic radius?  
(a) F (b) Cl  
(c) Cs (d) Mg
133. Covalent radius of nitrogen is 70 pm. Hence, covalent radius of boron is about  
(a) 60 pm (b) 110 pm  
(c) 50 pm (d) 40 pm

134. In which case bond length is shortened?  
 (a) When multiplicity occurs between atoms  
 (b) When electronegativities are different  
 (c) In both cases  
 (d) In none of the cases
135. Select correct statement about radius of an atom  
 (a) Values of van der Waals' radii are larger than those of covalent radii because the van der Waals' forces are much weaker than the forces operating between atoms in a covalently bonded molecule  
 (b) The metallic radii are smaller than the van der Waals' radii, since the bonding forces in the metallic crystal lattice are much stronger than the van der Waals' forces  
 (c) Both (a) & (b) are correct  
 (d) None of the above is correct
136. The separation of lanthanides in ion-exchange method is based on  
 (a) basicity of the hydroxides  
 (b) size of the hydrated ions  
 (c) size of the unhydrated ion  
 (d) the solubility of their nitrates
137. Select correct statement(s).  
 (a) Across a transition series, there is only a small decrease in atomic radius from one element to another due to very small increase in effective nuclear charge  
 (b) The rate of decrease in the size across the lanthanide series is less than the across the first transition series  
 (c) Both (a) & (b) are correct statements  
 (d) None of the above statement is correct
138. Select incorrect order of size of ions/atoms  
 (a)  $I^+ < I < I^-$  (b)  $Fe = Co = Ni$   
 (c)  $Ni < Cu < Zn$  (d) None is incorrect
139. Select correct alternate.  
 (a) Due to lanthanide contraction Zr and Hf have almost equal size  
 (b) Due to completion of 3d-subshell, the electronic charge density in this subshell becomes very high which increases the inter-electronic repulsion hence, size increases  
 (c) Both (a) & (b) are correct statements  
 (d) Both (a) & (b) are incorrect statements
140. The lanthanides contraction refers to  
 (a) ionic radius of the series  
 (b) valence electrons of the series  
 (c) the density of the series  
 (d) electronegativity
141. The second ionisation energy is always higher than the first ionisation energy because the  
 (a) ion becomes more stable attaining an octet or duplet configurations  
 (b) electron is more tightly bound to the nucleus in an ion  
 (c) electron is attracted more by the core electrons  
 (d) none of the above is the correct explanation
142. SI unit of  $IE$  is  
 (a)  $\text{kJ mol}^{-1}$  (b)  $\text{eV atom}^{-1}$   
 (c)  $\text{J mol}^{-1}$  (d)  $\text{kcal mol}^{-1}$
143. Which has maximum  $IE$ ?  
 (a) Mg (b)  $Mg^+$   
 (c)  $Mg^{2+}$  (d) Equal
144. Which pair represents incorrect first ( $IE$ )?  
 (a)  $Be > B$  (b)  $N > O$   
 (c)  $Li > Na$  (d)  $He > He^+$
145. Which represents alkali metals based on ( $IE$ )<sub>1</sub> and ( $IE$ )<sub>2</sub> values?
- |       | ( $IE$ ) <sub>1</sub> | ( $IE$ ) <sub>2</sub> |
|-------|-----------------------|-----------------------|
| (a) X | 100                   | 110                   |
| (b) Y | 95                    | 120                   |
| (c) Z | 195                   | 500                   |
| (d) M | 200                   | 250                   |
146. Which element has the highest first ( $IE$ )?  
 (a) N (b) Ne  
 (c) He (d) H
147.  $IE$  of an element does not depend on  
 (a) its nuclear charge (b) the shielding effect  
 (c) electron neutrality (d) penetration effect
148. The dominant factor in determining the  $IE$  of the elements on moving down the groups is its  
 (a) atomic radius  
 (b) effective nuclear charge  
 (c) both (a) and (b)  
 (d) none of the above
149. Select correct statement.  
 (a) ( $IE$ )<sub>1</sub> of the corresponding elements of 3d and 4d series are almost similar  
 (b) ( $IE$ )<sub>1</sub> of 5d-series elements are smaller than that of 3d and 4d-series elements  
 (c) both (a) & (b) are correct  
 (d) both (a) & (b) are incorrect
150. Higher values of ionisation energies of the 5d-transition elements are consistent with the  
 (a) relatively smaller effective nuclear charge  
 (b) relatively smaller size of their atoms  
 (c) relatively smaller penetration  
 (d) all the above are correct

### One or More Than One Options Correct

1. Stability of ions of Ge, Sn and Pb will be in order  
 (a)  $Ge^{2+} < Sn^{2+} < Pb^{2+}$  (b)  $Pb^{4+} < Sn^{4+} < Ge^{4+}$   
 (c)  $Sn^{2+} < Sn^{4+}$  (d)  $Pb^{4+} < Pb^{2+}$

2. The first element of a group in many ways differs from the other heavier members of the group. This is due to

- (a) the smaller size
- (b) the high electronegativity and high ionisation potential
- (c) the unavailability of  $d$ -orbitals
- (d) the higher shielding effect

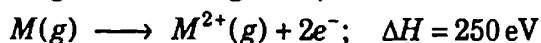
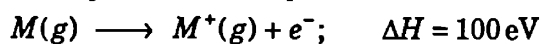
3. The factors that influence the ionisation energies are

- (a) the size of the atom
- (b) the charge on the nucleus
- (c) how effectively the inner electrons screen the nuclear charge
- (d) the atomic mass

4. Which is/are correct order of ionic mobility?

- (a)  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$
- (b)  $\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$
- (c)  $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+$
- (d)  $\text{K}^+ < \text{Na}^+ < \text{Li}^+$

5. Consider following ionisation steps:



Select correct statement(s).

- (a)  $(IE)_1$  of  $M(g)$  is 100 eV
- (b)  $(IE)_1$  of  $M^+(g)$  is 150 eV
- (c)  $(IE)_2$  of  $M(g)$  is 250 eV
- (d)  $(IE)_2$  of  $M(g)$  is 150 eV

6. An increase in both atomic and ionic radii with atomic number occurs in any group of the Periodic Table and in accordance with this the ionic radii of  $\text{Ti(IV)}$  and  $\text{Zr(IV)}$  ions are 0.68 Å and 0.74 Å respectively; but for  $\text{Hf(IV)}$  ion the ionic radius is 0.75 Å which is almost the same as that for  $\text{Zr(IV)}$  ion. This is due to

- (a) greater degree of covalency in compound of  $\text{Hf}^{4+}$
- (b) lanthanide contraction
- (c) difference in the coordination number of  $\text{Zr}^{4+}$  and  $\text{Hf}^{4+}$  in their compounds
- (d) actinide contraction

7. When an isotope undergoes K-capture, its mass number

- (a) remains the same while the atomic number increases by one
- (b) remains the same while the atomic number increases by two
- (c) remains the same while the atomic number decreases by one
- (d) as well as the atomic number decreases by one

8. The melting point of  $\text{RbBr}$  is  $682^\circ\text{C}$  while that of  $\text{NaF}$  is  $988^\circ\text{C}$ . The principal reason that the melting point of  $\text{NaF}$  is much higher than that of  $\text{RbBr}$  is that

- (a) the molar mass of  $\text{NaF}$  is smaller than that of  $\text{RbBr}$
- (b) the bond in  $\text{RbBr}$  has more covalent character than the bond in  $\text{NaF}$

(c) the difference in electronegativity between  $\text{Rb}$  and  $\text{Br}$  is smaller than the difference between  $\text{Na}$  and  $\text{F}$ .

(d) the internuclear distance,  $r_c + r_a$  is greater for  $\text{RbBr}$  than for  $\text{NaF}$

9. Select correct statement(s).

- (a)  $\text{Cs}^+$  is more highly hydrated than the other alkali metal ions
- (b) Among the alkali metals  $\text{Li}$ ,  $\text{Na}$ ,  $\text{K}$  and  $\text{Rb}$ , lithium has the highest melting point
- (c) Ionic mobility of  $\text{Li}^+$  is maximum among  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  ions
- (d) Ionisation potential of  $\text{Li}$  is smaller than that of  $\text{Na}$

10. Select correct statements.

- (a)  $\text{Ce}$ ,  $\text{Pr}$  and  $\text{Nd}$  are  $f$ -block elements
- (b)  $\text{Cu}$ ,  $\text{Pd}$  and  $\text{Ni}$  are  $d$ -block elements
- (c)  $\text{Cu}([\text{Ar}]3d^{10}4s^1)$  and  $\text{K}([\text{Ar}]4s^1)$  have been placed in  $s$ -block
- (d)  $\text{Si}$ ,  $\text{Ge}$  and  $\text{As}$  are metalloids

## Brain Twisters

1. Let us suppose that you have discovered a new element of atomic number 162, which you choose to name khalidium ( $\text{Kh}$ ). Assume that the normal order of filling of orbitals still prevails in the eighth period.

- (a) Write the full electron configuration of this element.
- (b) Write the valence electron configuration of this element and of its  $+2$  ion.
- (c) Note that a new type of orbital is used in  $\text{Kh}$  that is not used in any known atom. How many nodal planes will there be in a sketch of this type of orbital? How many nodal spheres will there be? Will the electrons in this type of orbital be good or poor at shielding the valence electrons of  $\text{Kh}$ ? Will electrons in this type of orbital be good or poor at penetrating the inner orbitals of  $\text{Kh}$ ?
- (d) Calculate  $Z^*$  for the outermost valence electron of  $\text{Kh}$ .
- (e) Using an estimated covalent radius of 150 pm calculate the Allred-Rochow electronegativity of  $\text{Kh}$ . Do you think that the Pauling electronegativity of  $\text{Kh}$  will be higher, lower, or about the same as this value?

2. How many joules of energy must be absorbed to convert to  $\text{Li}^+$  all the atoms present in 1.00 mg of gaseous  $\text{Li}$ ?  $(IE)_1$  of  $\text{Li}$  is  $320.3 \text{ kJ mol}^{-1}$ . ( $\text{Li} = 7$ )

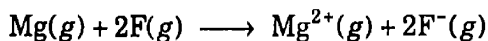
3. How much energy in kJ must be absorbed to ionise completely all the third shell electrons in a mole of gaseous phosphorus atoms?

$$(IE)_1 = 1012 \quad (IE)_2 = 1903 \quad (IE)_3 = 2912$$

$$(IE)_4 = 4957 \quad (IE)_5 = 6274 \quad (\text{values in } \text{kJ mol}^{-1})$$

Also express result in eV per atom.

4. Use (*IE*) and (*EA*) listed below to determine whether the following process is endothermic or exothermic :



$$(IE)_1 \text{ of Mg}(g) = 737.7 \text{ kJ mol}^{-1}$$

$$(IE)_2 \text{ of Mg}(g) = 1451 \text{ kJ mol}^{-1}$$

$$(EA) \text{ of F}(g) = -328 \text{ kJ mol}^{-1}$$

5. What is the value in  $\text{kJ mol}^{-1}$  which is equal to  $1 \text{ eV atom}^{-1}$ ?
6. A mixture contains F and Cl atoms. The removal of an electron from each atom of the sample requires  $284 \text{ kJ}$  while the addition of an electron to each atom of the mixture releases  $68.8 \text{ kJ}$ . Determine the mole % composition of the mixture.

|    | ( <i>IE</i> ) per atom             | ( <i>EA</i> ) per atom             |
|----|------------------------------------|------------------------------------|
| F  | $27.91 \times 10^{-22} \text{ kJ}$ | $-5.53 \times 10^{-22} \text{ kJ}$ |
| Cl | $20.77 \times 10^{-22} \text{ kJ}$ | $-5.78 \times 10^{-22} \text{ kJ}$ |

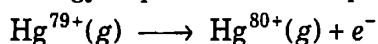
7. A hydrogen like ion is an ion containing only one electron. The energies of the electron in a hydrogen like ion are given by

$$E_n = -(2.18 \times 10^{-18}) Z^2 \left( \frac{1}{n^2} \right) \text{ joule}$$

where,  $n$  is the principal quantum number and  $Z$  is the atomic number of the element. Calculate the ionisation energy (in  $\text{kJ mol}^{-1}$ ) of the  $\text{He}^+$  ion.

8. Plasma is a state of matter consisting of positive gaseous ions and electrons. In the plasma state, a mercury atom could be stripped of its electrons and therefore would exist as  $\text{Hg}^{80+}$ .

Calculate energy required for the step



9. The atomic radius of K is  $216 \text{ pm}$  and that of  $\text{K}^+$  is  $133 \text{ pm}$ . Calculate the per cent decrease in volume that occurs when  $\text{K}(g)$  is converted to  $\text{K}^+(g)$ .

## Passage Comprehension Questions

### Passage 1

Following questions are based on  $\text{Sc}(Z = 21)$

- Out of  $\text{Sc}^{3+}$ ,  $\text{Sc}^{2+}$  and  $\text{Sc}^+$  paramagnetic as well coloured ions are
  - $\text{Sc}^+$ ,  $\text{Sc}^{2+}$
  - $\text{Sc}^+$ ,  $\text{Sc}^{3+}$
  - $\text{Sc}^{2+}$ ,  $\text{Sc}^{3+}$
  - all being  $d$ -block element
- For any  $1s$  electron,  $Z^*$  (effective nuclear charge is)
  - 21.0
  - 20.65
  - 16.85
  - 9.75
- For  $3d$ -electron,  $Z^*$  is
  - 20.65
  - 16.85
  - 9.75
  - 3.00

### Passage 2

Following rule in general, classifies  $p$ -block elements into metals, non-metals and metalloids (where  $P$  is the period and  $N$  the valence electrons)

$(P + 1) > N$ , the element would be metal

$(P + 1) < N$ , the element would be non-metal

$(P + 1) = N$ , the element would be metalloid

Answer the following questions

- Metalloid will be out of elements with atomic number 13, 14, 15, 16
  - 13
  - 14
  - 15
  - 16
- Metals will be out of 13, 31, 35, 54
  - 13, 31
  - 31, 35
  - 35, 54
  - 13, 54
- Non-metals will be out of 13, 31, 35, 54
  - 13, 31
  - 31, 35
  - 35, 54
  - 13, 54
- Which will find use in semi-conductors?
  - 5, 13
  - 5, 14
  - 13, 14
  - 14, 16

### Passage 3

In the following table  $I_1$ ,  $I_2$  and  $I_3$  of the main group elements in 2nd period have been given.

|       | Li    | Be    | B    | C    | N    | O    | F    | Ne   |
|-------|-------|-------|------|------|------|------|------|------|
| $I_1$ | 513   | 899   | 801  | 1086 | 1402 | 1314 | 1681 | 2080 |
| $I_2$ | 7298  | 1757  | 2427 | 2352 | 2856 | 3388 | 3374 | 3952 |
| $I_3$ | 11815 | 14848 | 3660 | 4620 | 4578 | 5300 | 6050 | 6122 |

Answer the following question based on the above table.

- There is increase in ionisation energy along a period going Li to Ne, but  $I_1$  of B is less than that of Be. This is due to
  - valence electron in B is in  $2p$ -orbital of higher energy than that of Be in  $2s$ -orbital of lower energy
  - removal of paired electron in Be requires higher energy than that of removal of unpaired electron in B.
  - both (a) & (b) above
  - None of the above
- We observe that  $I_1$  of Be  $>$   $I_1$  of B but  $I_2$  of Be  $<$   $I_2$  of B. Select correct explanation(s).
  - Electron in Be is paired while in B, electron is unpaired, hence  $I_1$  of Be  $>$   $I_1$  of B
  - Electron in  $\text{Be}^+$  is unpaired while in  $\text{B}^+$ , electron is paired, hence  $I_2$  of Be  $<$   $I_2$  of B.
  - Both (a) & (b) above
  - None of the above

3. There occurs a fall while going from N to O.

It is due to

(a) stable configuration of N  $\uparrow \uparrow \uparrow$

(b) higher atomic number of O

(c) stable configuration of O  $\uparrow \downarrow \uparrow \downarrow$

(d) lone pairs on O.

### Passage 4

The sums of first and second ionisation energies and those of third and fourth ionisation energies (in  $\text{MJ mol}^{-1}$ ) of nickel and platinum are

|    | $(IE)_1 + (IE)_2$ | $(IE)_3 + (IE)_4$ |
|----|-------------------|-------------------|
| Ni | 2.49              | 8.80              |
| Pt | 2.66              | 6.70              |

Based on this information, answer the following questions. Name of the metal (Ni or Pt) which can more easily form compounds in its +4 oxidation state.

1. Most common oxidation states of Ni and Pt are respectively

- (a) +2, +2 (b) +4, +2  
(c) +2, +4 (d) +4, +4

2. Which is most stable complex of Ni?

- (a)  $[\text{Ni}(\text{CN})_4]^{2-}$  (b)  $[\text{Ni}(\text{CN})_6]^{2-}$   
(c)  $[\text{Ni}(\text{CN})_3]^-$  (d)  $[\text{Ni}(\text{CO})_6]$

3. Which is least stable complex of Pt?

- (a)  $\text{K}_2[\text{PtCl}_6]$  (b)  $[\text{Pt}(\text{en})_3]\text{Cl}_4$   
(c)  $\text{K}_2[\text{PtCl}_4]$  (d)  $\text{K}_2[\text{Pt}(\text{C}_2\text{O}_4)_3]$

### Passage 5

The  $(IE)_1$  and the  $(IE)_2$  in  $\text{kJ mol}^{-1}$  of a few elements designated by Roman numerals are shown below:

| Element | $(IE)_1$ | $(IE)_2$ |
|---------|----------|----------|
| A       | 2372     | 5251     |
| B       | 520      | 7300     |
| C       | 900      | 1760     |
| D       | 1680     | 3380     |

Based on above information, answer the following questions:

1. Which of the above elements is likely to be a reactive metal?

- (a) A (b) B  
(c) C (d) D

2. Which of the above elements is likely to be a reactive non-metal?

- (a) A (b) B  
(c) C (d) D

3. Which represents a noble gas?

- (a) A (b) B  
(c) C (d) D

4. Which of the above elements forms a stable binary halide of the formula  $\text{MX}_2$ ?

- (a) A (b) B  
(c) C (d) D

### Passage 6

The heats of formation ( $\Delta H_f^\circ$ ) of the oxides of the third period, sodium to chlorine, are in  $\text{kJ mol}^{-1}$

|                       |              |                         |                |                           |               |                         |
|-----------------------|--------------|-------------------------|----------------|---------------------------|---------------|-------------------------|
| $\text{Na}_2\text{O}$ | $\text{MgO}$ | $\text{Al}_2\text{O}_3$ | $\text{SiO}_2$ | $\text{P}_4\text{O}_{10}$ | $\text{SO}_3$ | $\text{Cl}_2\text{O}_7$ |
| -416                  | -602         | -1676                   | -911           | -2984                     | -395          | +250                    |

Based on these data, answer the following questions

1. Which oxide has maximum negative heat of formation per oxygen atom?

- (a)  $\text{P}_4\text{O}_{10}$  (b)  $\text{Al}_2\text{O}_3$   
(c)  $\text{Na}_2\text{O}$  (d)  $\text{MgO}$

2. Most stable and least stable oxides are

- (a)  $\text{P}_4\text{O}_{10}$ ,  $\text{Cl}_2\text{O}_7$  (b)  $\text{Na}_2\text{O}$ ,  $\text{Cl}_2\text{O}_7$   
(c)  $\text{MgO}$ ,  $\text{Cl}_2\text{O}_7$  (d)  $\text{Cl}_2\text{O}_7$ ,  $\text{MgO}$

3. Stability order of the above oxides is

- (a)  $\text{Cl}_2\text{O}_7 < \text{SO}_3 < \text{P}_4\text{O}_{10} < \text{SiO}_2 < \text{Al}_2\text{O}_3 < \text{MgO} < \text{Na}_2\text{O}$   
(b)  $\text{Cl}_2\text{O}_7 < \text{SO}_3 < \text{P}_4\text{O}_{10} < \text{Na}_2\text{O} < \text{SiO}_2 < \text{Al}_2\text{O}_3 < \text{MgO}$   
(c)  $\text{Cl}_2\text{O}_7 < \text{SO}_3 < \text{Na}_2\text{O} < \text{MgO} < \text{SiO}_2 < \text{Al}_2\text{O}_3 < \text{P}_4\text{O}_{10}$   
(d)  $\text{P}_4\text{O}_{10} < \text{Al}_2\text{O}_3 < \text{SiO}_2 < \text{MgO} < \text{Na}_2\text{O} < \text{SO}_3 < \text{Cl}_2\text{O}_7$

### Passage 7

Consider following table comparing ionic radius

| Ion $\rightarrow$         | $\text{N}^{3-}$ | $\text{O}^{2-}$ | $\text{F}^-$ | $\text{Na}^+$ | $\text{Mg}^{2+}$ |
|---------------------------|-----------------|-----------------|--------------|---------------|------------------|
| Number of electron        | 10              | 10              | 10           | 10            | 10               |
| Number of nuclear protons | 7               | 8               | 9            | 11            | 12               |
| Ionic radius (pm)         | 146             | 140             | 133          | 98            | 79               |

Answer the following questions.

1. Select correct alternate(s) in terms of size.

- (a)  $\text{Na} > \text{Na}^+$  (b)  $\text{Mg} > \text{Mg}^+ > \text{Mg}^{2+}$   
(c)  $\text{F}^- > \text{F}$  (d)  $\text{O}^{2-} > \text{O}^- > \text{O}$

2. All the above species are isoelectronic but they differ in size. It is due to

- (a) increase in number of protons  
(b) removal of valence shell  
(c) decrease in repulsive force  
(d) addition of additional shell

### Passage 8

The singly-bonded metallic radius of Na is 157 pm. Assume that the increment between radii of different magnitudes is 60 pm. Answer the following questions.

- The covalent radius of Na is  
(a) 157 pm (b) 97 pm  
(c) 217 pm (d) 267 pm
- Ionic radius of  $\text{Na}^+$  is  
(a) 157 pm (b) 97 pm  
(c) 217 pm (d) 267 pm
- Ionic radius of  $\text{Na}^-$  is  
(a) 157 pm (b) 97 pm  
(c) 217 pm (d) 267 pm
- van der Waals' radius of Na is  
(a) 157 pm (b) 97 pm  
(c) 217 pm (d) 267 pm

### Assertion & Reason

Codes :

- Both **A** and **R** are true and **R** is the correct explanation of **A**.
  - Both **A** and **R** are true but **R** is not the correct explanation of **A**.
  - A** is true but **R** is false.
  - A** is false but **R** is true.
- Assertion (A)** : Tin exhibits +2 and +4 oxidation states only and not +3 oxidation state.  
**Reason (R)** : Inert pair effect of electrons in the *s*-orbital is responsible.
  - Assertion (A)** :  $\text{Na}^+$  and  $\text{Al}^{3+}$  are isoelectronic but the magnitude of ionic radius of  $\text{Al}^{3+}$  is less than that of  $\text{Na}^+$ .  
**Reason (R)** : The magnitude of effective nuclear charge of the outershell electrons in  $\text{Al}^{3+}$  is greater than that in  $\text{Na}^+$ .
  - Assertion (A)** : The atomic radii of the elements of the oxygen family are smaller than the atomic radii of the corresponding elements of the nitrogen family.  
**Reason (R)** : The members of the oxygen family are more electronegative and thus have lower values of nuclear charge than those of the nitrogen family.
  - Assertion (A)** :  $\text{PbCl}_2$  is more stable than  $\text{PbCl}_4$ .  
**Reason (R)** :  $\text{PbCl}_4$  is powerful oxidising agent.
  - Assertion (A)** : The mobility of sodium ion is lower than that of potassium ion.  
**Reason (R)** : The ionic mobilities depend upon the effective radius of the ion.

**6. Assertion (A)** : Sc ( $Z = 21$ ) is placed in *d*-block elements.

**Reason (R)** : Last filling electron goes into 3*d*-suborbit.

**7. Assertion (A)** : Ionisation energy decreases on moving down the group.

**Reason (R)** : Force of attraction between electrons and nucleus decreases on moving down the group.

**8. Assertion (A)** : Li and Mg shows diagonal relationship.

**Reason (R)** : Li and Mg are diagonal to each other in the Periodic Table.

**9. Assertion (A)** : Fluorine has a less negative electron affinity than chlorine.

**Reason (R)** : There is relatively greater effectiveness of 2*p*-electrons in the small F atom to repel the additional electron entering the atom than to 3*p*-electrons in the larger Cl atom.

**10. Assertion (A)** :  $\text{SnCl}_2$  is a reducing agent.

**Reason (R)** :  $\text{SnCl}_2$  reduces  $\text{FeCl}_3$  to  $\text{FeCl}_2$  and  $\text{HgCl}_2$  to Hg.

### True & False

- Electron affinity of Cl is greater than that of F.
- $\text{Al}_2\text{O}_3$  in aqueous NaOH forms  $\text{Na}[\text{Al}(\text{OH})_4]$ .
- CO is an acidic oxide.
- $\text{PbO}_2$  is a reducing agent.
- Ionic mobility of  $\text{Li}^+$  is greater than that of  $\text{Na}^+$ .
- $\text{B}_2\text{O}_3$  is an amphoteric oxide.
- ZnO is amphoteric.
- LiCl can be used to control humidity.
- (*IE*)<sub>2</sub> of H is less than that of He.
- First long period has 18 elements.
- $\text{Na}_2\text{CO}_3$  is thermally stable but  $\text{Li}_2\text{CO}_3$  is not.
- Atomic size of Fe > Co > Ni.
- Atomic size of Ne > F.
- (*IE*)<sub>2</sub> of Li is maximum in the Periodic Table.
- The noble gas core together with  $(n - 1)d^{10}$  electrons is called pseudo-noble gas core.
- Helium is the most unreactive element of the Periodic Table.

## Fill in the Blanks

- ..... is the lightest of all metals.
- ..... is the only non-metallic element which is liquid at room temperature.
- Two atoms of similar electronegativity would be expected to form a ..... compound.
- Of the halide ions, ..... is the most powerful reducing agent.
- As the atomic radius increases, ionisation energy .....
- The element having electronic configuration  $1s^2 2s^2 2p^6 3s^2 3p^2$  has valency .....
- The substance which loses electrons is said to be ..... and the substance which gains electrons is said to be .....
- Elements of group ..... have greater tendency to form positive ions than elements of group IIA.
- An element which can exist as a positive ion in acidic solution and also as a negative ion in basic solution is said to be .....
- On Mulliken scale, the average of ionisation energy and electron affinity is called .....
- ..... is the most electronegative element in the Periodic Table.
- Ionic mobility of  $Al^{3+}$  is ..... than that of  $Na^+$ .
- $(IE)_1$  of Be is ..... than that of B but  $(IE)_2$  of Be is ..... than that of B.
- Electron affinity of F ..... than that of Cl.
- In aqueous solution ..... is the best reducing agent among alkali metals.

## Matrix-Match Type Questions

### I. Only One Correct

- Match atomic number of elements (in List I) with position of elements in the Periodic Table (in List II).

| List I | List II    |
|--------|------------|
| A. 19  | 1. p-block |
| B. 22  | 2. f-block |
| C. 32  | 3. d-block |
| D. 64  | 4. s-block |

- Match the type of elements (in List I) with the corresponding electronic configuration (in List II).

| List I                       | List II                                       |
|------------------------------|-----------------------------------------------|
| A. Inert gas elements        | 1. $ns^1$ to $ns^2 np^5$                      |
| B. Main group elements       | 2. $1s^2$ to $ns^2 np^6$                      |
| C. Transition elements       | 3. $(n-2)f^{1-14} (n-1)s^2 p^6 d^{1-10} ns^2$ |
| D. Inner transition elements | 4. $(n-1)d^{1-9} ns^2$                        |
|                              | 5. $(n-1)d^{10} ns^2$                         |

- Match the classification (in List I) with the element (in List II).

| List I                  | List II |
|-------------------------|---------|
| A. Alkaline earth metal | 1. Rb   |
| B. Radioactive element  | 2. As   |
| C. Alkali metal         | 3. Mg   |
| D. Metalloid            | 4. Fr   |

- Match the element (in List I) with its unique properties (in List II).

| List I | List II                      |
|--------|------------------------------|
| A. F   | 1. Maximum ionisation energy |
| B. Cl  | 2. Maximum electronegativity |
| C. Fe  | 3. Maximum electron-affinity |
| D. He  | 4. Recently named by IUPAC   |
| E. Ds  | 5. Variable valency          |

- Match the atomic number (in List I) with its IUPAC nomenclature (in List II).

| List I | List II |
|--------|---------|
| A. 105 | 1. Uuh  |
| B. 107 | 2. Uun  |
| C. 109 | 3. Uns  |
| D. 110 | 4. Unp  |
| E. 116 | 5. Une  |

### II. One or More Correct

- Match the element in Column I with its corresponding property (ies) in Column II.

| Column I | Column II                            |
|----------|--------------------------------------|
| A. F     | 1. Maximum electron-affinity         |
| B. Cl    | 2. Maximum electronegativity         |
| C. Br    | 3. Exists as $X_2$ in liquid state   |
| D. I     | 4. Exists as $X_2$ in solid state    |
| E. At    | 5. $X_2$ sublimates on heating       |
|          | 6. $X_2$ is the best oxidising agent |
|          | 7. Radioactive element               |

2. Match the oxide in Column I with its corresponding property (ies) in Column II.

| Column I                   | Column II                |
|----------------------------|--------------------------|
| A. $\text{Na}_2\text{O}$   | 1. Soluble in HCl        |
| B. $\text{MgO}$            | 2. Soluble in NaOH       |
| C. $\text{Al}_2\text{O}_3$ | 3. Turns blue litmus red |
| D. $\text{SiO}_2$          | 4. Turns red litmus blue |
| E. $\text{P}_2\text{O}_5$  | 5. Giant molecule        |
| F. $\text{SO}_3$           | 6. Acid-rain             |

## Integer Answer Types

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the ORS have to be darkened. For example, if the correct answers to question number X, Y, Z and W (say) are 6, 0, 9 and 2, respectively

| X | Y | Z | W |
|---|---|---|---|
| ① | ① | ① | ① |
| ② | ② | ② | ② |
| ③ | ③ | ③ | ③ |
| ④ | ④ | ④ | ④ |
| ⑤ | ⑤ | ⑤ | ⑤ |
| ⑥ | ⑥ | ⑥ | ⑥ |
| ⑦ | ⑦ | ⑦ | ⑦ |
| ⑧ | ⑧ | ⑧ | ⑧ |
| ⑨ | ⑨ | ⑨ | ⑨ |

### Set I

- Magnetic moment of an element is 1.73. Thus, unpaired electron can be .....
- Maximum oxidation state shown by Mn is .....
- Electronegativity =  $\frac{(IP) + (EA)}{N}$ .  
This  $N = \dots\dots\dots$
- Stability of Tl is maximum when its valency is .....
- Catention is maximum for the element with atomic number .....
- Lanthanides have been placed in period .....
- Actinides have been placed in period .....
- Number of unpaired electron in Gd(64) is .....

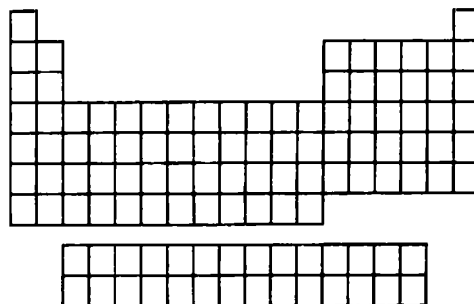
### Set II

- Effective nuclear charge of an element with three valence electrons in 2.60. Thus, atomic number of the element is .....
- Number of amphoteric oxides out of  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{BeO}_2$  and  $\text{CaO}$  is .....
- Maximum electron affinity is shown by the species at serial number.  
(1) O (2) F (3)  $\text{Cl}^-$  (4) He (5) N
- Diatomic molecule is formed by the element at serial number (1) and at serial number .....  
(1)  $[\text{Ne}]3s^2 3p^1$  (2)  $[\text{Ne}]3s^1$   
(3)  $[\text{Ne}]3s^2$  (4)  $[\text{He}]2s^2 2p^3$   
(5)  $[\text{Ne}]3s^2 3p^6$  (6) [Ne]

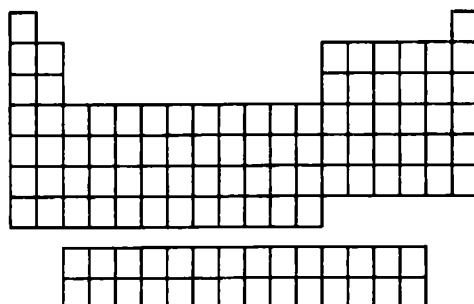
- An ionic compound is formed of the type XY from X with electronic configuration  $ns^1$  and Y with valence shell electrons .....
- Maximum oxidation state shown by chalcogens is .....
- Ionisation energy of  $M^{3+}$  is 217.6 eV compared to that of  $\text{He}^+$  (54.4 eV). Thus, atomic number of  $M^{3+}$  is .....
- Semi-conductor with minimum value of atomic number is .....

## Test Yourself on Periodic Table

- Test your knowledge of the Periodic Table by indicating where on the blank outline elements that meet the following descriptions appear:
  - Elements with the valence-shell ground-state electron configuration  $ns^2 np^5$
  - An elements whose fourth shell contains two  $p$ -electrons
  - An element with the ground-state electron configuration  $[\text{Ar}] 4s^2 3d^{10}$



- Circle the approximate part or parts of the Periodic Table where the following elements appear :
  - Elements with the smallest values of  $(IE)_1$
  - Elements with the largest atomic radii
  - Elements with the most negative values of EA



- Test your knowledge of the Periodic Table by indicating approximately where on the blank outline the following elements appear :



- (a) Main groups                      (b) Halogens  
 (c) Alkali metals                  (d) Noble gases  
 (e) Alkaline earths metals (f) Group 3A elements  
 (g) Lanthanides
4. Look at the location of elements *A*, *B*, *C*, and *D* in the following Periodic Table :
- (a) Write the formula of the oxide that has each of these elements in its highest oxidation state.  
 (b) Classify each oxide as basic, acidic, or amphoteric.  
 (c) Which oxide is the most ionic? Which is the most covalent?  
 (d) Which of these oxides are molecular? Which are solids with an infinitely extended three-dimensional crystal structure?

- (e) Which of these oxides has the highest melting point?

Which has the lowest melting point?

5. Look at the location of elements *A*, *B*, *C*, and *D* in the following Periodic Table:

- (a) Write the formula of the simplest binary hydride of each element.  
 (b) Classify of these hydride as ionic, covalent or interstitial.  
 (c) What are the oxidation states of hydrogen and other elements in the hydrides of *A*, *C* and *D*?

# Answers & Solutions

## Master Exercises

### Exercise 1

#### Short Answer Type Questions

1. Melting point is a reflection of the attractive force which holds the constituent particles of the solid element. In metals, this force depends primarily on the size and nature of packing of the atoms in the crystal and on the contribution of valence shell electrons in bonding. The lower melting point of Ag suggests that *d*-electrons in metallic bonding are involved to a smaller extent compared to Cu and Au. This is confirmed by the fact that common oxidation of Ag is +1 while that of Cu and Au are +2 and +3 respectively.

The lower melting points of Zn—Cd—Hg in comparison to Cu—Ag—Au also indicate that there is contraction of *d*-orbital from increasing nuclear charge; in Hg this is reinforced by still poor shielding by the *f*-electrons.

2. This is general formula to calculate  $Z^*$  directly by use of valence electrons  $n$ .

| Element | Z | EC               | $n$ (valence electrons) | $Z^* = 0.65[1 + n]$ |
|---------|---|------------------|-------------------------|---------------------|
| Li      | 3 | $1s^2 2s^1$      | 1                       | 1.30                |
| Be      | 4 | $1s^2 2s^2$      | 2                       | 1.95                |
| B       | 5 | $1s^2 2s^2 2p^1$ | 3                       | 2.60                |
| C       | 6 | $1s^2 2s^2 2p^2$ | 4                       | 3.25                |

3. (a) H being least electronegative, its oxidation number is taken as = +1.

and O being most electronegative, its oxidation number is taken as = -2. Take oxidation number of I =  $x$

Thus,

$$\begin{array}{c} \text{H}_2\text{IO}_6^{3-} \\ \uparrow \uparrow \\ +2 + x - 12 = -3 \\ x = +7 \end{array}$$

- (b) Oxygen being more electronegative than sulphur is assigned oxidation number = -2

and oxidation number of sulphur =  $x$

Thus,

$$\begin{array}{c} \text{S}_3\text{O}_6^{2-} \\ \uparrow \\ 3x - 12 = -2 \end{array}$$

- (c)  $\text{Na}_2\text{O}_2$   $x = 3.33$

$$\begin{array}{c} \uparrow \\ +2 + 2x = 0 \\ x = -1 \end{array}$$

4. (a), (b)  $5g < 5f < 5d < 5p < 5s$   
 (c)  $5s < 5p < 5d < 5f < 5g$   
 5. (a) 157 pm (b) 97 pm (c) 217 pm (d) 217 pm  
 6. (a)  $F < C < Li < Ne$  (Ne has van der Waal's radius)  
 (b)  $Be < Ca < Ba < Ra$   
 (c)  $B < Al \approx Ga < In \approx Tl$   
 (d)  $V < Nb = Ta \approx Db$   
 7. (a) increase (b) decrease (c) less rapidly  
 (d) stay the same; decreases; less rapidly  
 (e) increase; increase, less rapidly

#### Analytical Questions

1.  $\text{Ca}^{2+} < \text{K}^+ < \text{Ar} < \text{Cl}^- < \text{S}^{2-}$   
 2. (a) In (b) C (c) Cs (d) I (e) Xe  
 3. (a) 6 (b) 8 (c) 7 (d) 1 (e) 2 (f) 4  
 4. (a) As (b) Sr (c) Cs (d) Xe (e) C (f) Hg  
 5.  $\text{Cs} < \text{Sr} < \text{As} < \text{S} < \text{F}$   
 6. (d) < (a) < (b) < (c) < (e)  
 7. (a) most metallic : Ba (b) most non-metallic : S  
 (c) intermediate  $(IE)_1$  : Bi  
 8.  $\text{Rb} > \text{Ca} > \text{Sc} > \text{Fe} > \text{Te} > \text{Br} > \text{O} > \text{F}$   
 9. Diamagnetic (which does not have unpaired electrons) :  $\text{K}^+, \text{Zn}^{2+}, \text{Cd}, \text{Sn}^{2+}$   
 Paramagnetic (which has unpaired electrons) :  $\text{Cr}^{3+}, \text{Co}^{3+}$   
 10. Noble gas has  $Z = 118$  and alkali metal  $Z = 119$ ; atomic weight should be about 310.  
 11. 101 102 103 104 105 106 107 108 109  
 Unu Unb Unt Unq Unp Unh Uns Uno Une  
 12. (a) 4 (b) 3 (c) 1 (d) 2 (e) 1 (f) 2  
 13.
- |        | Covalent radius | $(IE)_1$ |
|--------|-----------------|----------|
| (b) Al | 125 pm > Ge     | 577 < Ge |
| (c) In | 150 pm > Ge     | 558 < Ge |
| (d) Se | 114 pm < Ge     | 941 > Ge |
14. (a) Ba (b) Al (c) Cl (d) N  
 15. Oxygen is more electronegative than chlorine and cannot be oxidised by it.

16. Outer shell electronic configuration :
- $ns^2np^3$

(Three electrons less than octet)

Number of electrons required to fill the valence shell = 3

Hence,  $X^{3-}$  has configuration =  $ns^2np^6$  $X^{3-}$  has stable nearest inert gas configuration hence most negative oxidation state = -3

17. (a) Ca (b) Cl (c)
- $N_2O_3$
- (d) Al (e) N (f) Br (g) BaO

(h) CsOH (i)  $B(OH)_3$  (j) S (k) RbCl (l) O(m)  $Al(OH)_3$  (n)  $KNO_2$  (o)  $Li^+$  (p) Be (q) F(r)  $O^-$  (s) O (t)  $Na^+$  (u) Ne (v) Hg (w)  $Al_2O_3$ (x)  $B_2O_3$  (y)  $In_2O_3$  (z) carbon (diamond)

18. (a) -V (b) -III (c) -I (d) -IV (e) -II

19. a fuming red liquid —
- $Br_2$

a dark metallic looking solid —  $I_2$ a pale yellow gas —  $Cl_2$ yellow green gas —  $F_2$ 

20. X : Sn or Pb, Y : P, Z : alkali metal

21. (a) Ge, (b) S, (c) Tl, (d) Ne,

(e) Se  $c < a < e < b < d$ 

22. (a) a non-metal : III

(b) an alkali metal : I

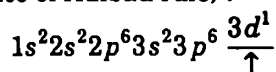
(c) an alkaline earth metal : II

23. IUPAC name : Uue, Chloride :
- $MCl$
- , Oxide :
- $M_2O$

## Exercise 2

### Only One Option Correct

1. K-19 (in absence of Aufbau rule) :

last-filling electron goes into  $d$ -orbital. Thus,  $d$ -block element.

Thus, (c)

- 2.
- $I_3$
- is very high indicating +2 oxidation state is most stable. Thus, element is of group 2.

Thus, Be.

Thus, (a)

- 3.
- $\left. \begin{array}{l} N(7) \\ \text{and } O^+(8) \end{array} \right\} 1s^2 2s^2 \underbrace{2p_x^1 2p_y^1 2p_z^1}_{\text{Maximum multiplicity most stable}}$

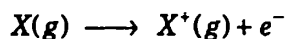
 $O] 1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ (IP) is dependent on the value of  $Z$ . $Z$  of  $O^+(8) > Z$  of  $N(7)$ Thus, (IP) of  $O^+ > N$ 

Na with one valence electron has least IP

Thus, (c)

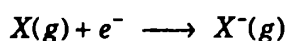
4. Let
- $IP = I$

$$EA = E$$



$$\frac{N_0}{2} I = E_1$$

$$\therefore I = \frac{2E_1}{N_0}$$



$$\frac{N_0 E}{2} = E_2$$

$$\therefore E = \frac{2E_2}{N_0}$$

Thus, (b)

5. Smaller cation, larger charge, larger hydration

Size of cation  $Na^+ > Mg^{2+} > Al^{3+} > Si^{4+}$  Minimum sizeCharge  $\longrightarrow$  Maximum chargeThus,  $SiCl_4$  is maximum hydrated.

Thus, (d)

6. (c) 7. (b)

8. Repulsive force are balanced by attractive force, thus, (c)

9. (d) 10. (c)

|     |    |    |                      |                    |
|-----|----|----|----------------------|--------------------|
| 11. | O  | F  | $F < O$              | $I > Br > F$       |
|     | S  | Cl | Thus, $F^- < O^{2-}$ | $I^- > Br^- > F^-$ |
|     | Se | Br | $Se > O$             |                    |
|     |    | I  | $Se^{2-} > O^{2-}$   |                    |

 $I > Se$  $\therefore I^- > Se^{2-}$ Thus,  $I^- > Se^{2-} > Br^- > O^{2-} > F^-$ 

Thus, (d)

12. (d)

13. Maximum hydrated ion is
- $Al^{3+}$
- .

Thus, (b)

14. Smaller cation, larger anion, maximum polarising power

Thus,  $Te^{2-}$ 

Thus, (d)

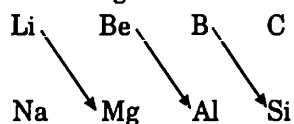
15. (d) 16. (d)

17. (a) Li—Mg diagonal relationship

(b)  $Na—K$ (c)  $Ca—Mg$  same group(d)  $B—Al$ 

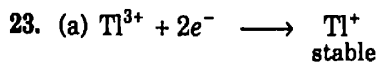
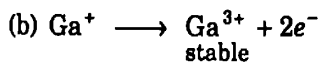
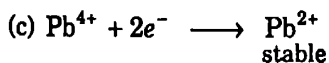
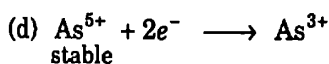
Thus, (a)

18. Except (d) all show diagonal relationship.



Thus, (d)

19. (a) 20. (d) 21. (b) 22. (d)

 $\text{Tl}^{3+}$  is an oxidising agent thus correct. $\text{Ga}^+$  is a reducing agent thus correct. $\text{Pb}^{4+}$  is an oxidising agent thus correct. $\text{As}^{5+}$  cannot be reducedThus,  $\text{As}^{5+}$  salts are not oxidising agent.

Thus, (d)

24. (d) 25. (a)

26. Smaller cation, larger anion, larger charge (on cation or anion)

greater the polarising power,

larger the covalent nature

smaller the melting point

 $\text{Na}^+$  (same), charge on cation, anion—same

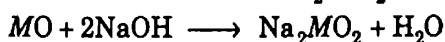
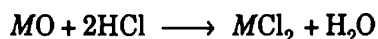
Thus, size of anion will decide polarising power.

Size :  $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$ Polarising power :  $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$ Covalent  $\text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI}$ Melting point  $\text{NaF} > \text{NaCl} > \text{NaBr} > \text{NaI}$ 

Thus, (a)

27. (b)

- 28.
- $\text{BeO}$
- ,
- $\text{SnO}$
- ,
- $\text{ZnO}$
- , all are soluble in alkalis as well as in acids, thus are amphoteric oxides.



Thus, (d)

29. Polarising power of
- $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Ba}^{2+}$

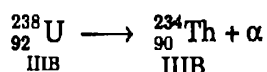
Thus, ionic nature of  $\text{BeCl}_2 < \text{MgCl}_2 < \text{CaCl}_2 < \text{BaCl}_2$ 

Thus, (a)

30. Stable configuration with all unpaired electron in
- $f$
- orbital is
- $[\text{Xe}] 6s^2 4f^7 5d^1$

Thus, (b)

31. Element (58-71) and (90-103) are placed in IIIB.



Thus, (a)

- 32.
- $\text{O} > \text{F}$

 $\text{O}^- > \text{F}^-$  Thus,  $\text{O}^{2-} > \text{O}^- > \text{F}^- > \text{F}$  $\text{O}^{2-} > \text{F}^-$ 

Thus, (a)

33. (c) 34. (a)

35. Due to empty
- $d$
- orbital, screening effect decreases, hence tendency to attract electron increases.

Thus, (c)

36. Oxides of C is a giant molecule indicating covalent nature

Oxide of B is amphoteric

Oxide of A is ionic

Thus, A is largest in size.

Thus, atomic number of A is least

 $A < B < C$ 

Thus, (a)

| 37. | Z | $r_n$ | (IE) | (EN) | Oxidising power |
|-----|---|-------|------|------|-----------------|
| F   |   |       |      |      | $\text{F}_2$ ↑  |
| Cl  |   |       |      |      | $\text{Cl}_2$   |
| Br  |   |       |      |      | Br              |
| I   |   |       |      |      | $\text{I}_2$ ↓  |

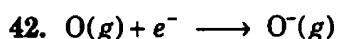
Thus, (a)

38. (a)
- $-\text{F}$
- (b)
- $-\text{Ne}$
- zero (EA) (c)
- $-\text{Cl}$

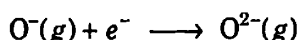
(d)  $-\text{Ar}$  zero (EA)(c)  $\text{Cl} > \text{F}$  due to empty  $d$ -orbital in Cl

Thus, (c)

39. (b) 40. (c) 41. (d)



EA = -ve



EA = +ve

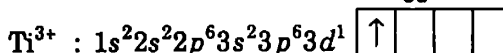
Thus, (b)

43. Ionic radii of
- $\text{O}^{2-} > \text{F}^- > \text{Na}^+ > \text{Mg}^{2+}$

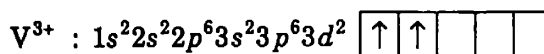
We take van der Waals' radius of Ne which should have maximum size.

Thus, (a)

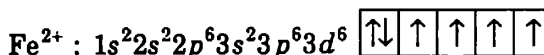
44. (a) 45. (d)

unpaired electron zero  
3d

1



2



4

- 47.
- $\text{I} > \text{II} > \text{III}$

Thus, (a)

48. (d) 49. (b)

50. (IV) B contains C, Si, Ge, Sn, Pb

Ge, Sn, Pb are strongly electropositive.

Thus, (d)

51. (d)

52. I.P. of Li &gt; Na

Thus, Na falls below Li

Thus, (c)

|                              | Be                 | B                    |
|------------------------------|--------------------|----------------------|
| 53. $I_1$ of Be > $I_1$ of B | $1s^2 2s^2$        | $1s^2 2s^2 2p^1$     |
| $I_2$ of Be < $I_2$ of B     | $\downarrow I_1$   | $\downarrow I_1$     |
| $I_3$ of Be > $I_3$ of B     | $1s^2 2s^1 (Be^+)$ | $1s^2 2s^2 (B^+)$    |
|                              | $\downarrow I_2$   | $\downarrow I_2$     |
|                              | $1s^2 (Be^{2+})$   | $1s^2 2s^1 (B^{2+})$ |
|                              | $\downarrow I_3$   | $\downarrow I_3$     |
|                              | $1s^1 (Be^{3+})$   | $1s^2 (B^{3+})$      |

Thus, (b) is incorrect.

Thus, (b)

54. smaller the size (P) of the ion

larger the charge (Q)

then larger the hydration (R) and

thus, smaller the ionic mobility (S)

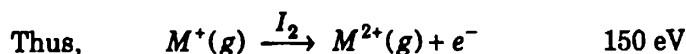
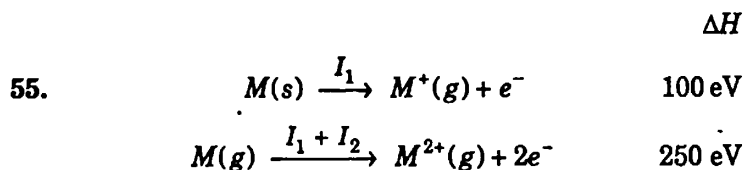
|        | P            | Q          | R          | S          |
|--------|--------------|------------|------------|------------|
| $Li^+$ | $\downarrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ |
| $Na^+$ | $\downarrow$ | same       |            |            |
| $K^+$  | $\downarrow$ |            |            |            |
|        | max          |            | max        |            |

Thus, (a) is true

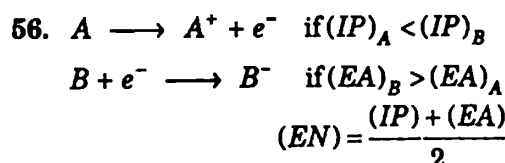
|   | $Na^+$       | $Mg^{2+}$     | $Al^{3+}$     |
|---|--------------|---------------|---------------|
| P | $\leftarrow$ |               |               |
| Q |              | $\rightarrow$ |               |
| R |              |               | $\rightarrow$ |
| S |              |               | $\rightarrow$ |
|   | max          |               | max           |

Thus, (b) is also true

Thus, (c)

Thus, (a) is true, (b) is also true ( $I_1$  of  $M^+(g)$  is  $I_2$  of  $M(g)$ )

Thus, (c) is incorrect

 $A^+ B^-$  is formedif  $(EN)_A < (EN)_B$ 

Thus, (c)

$$57. (EN) = \frac{(IP) + (EA)}{2}$$

$$(EA) = 2(EN) - (IP)$$

$$= 2E_1 - E_2$$

Thus, (a)

58. (c) due to inert-pair effect.

59. Copper forms only basic oxide

Thus, (b)

60. (IP) of N &gt; O

Thus, (a)

61. In case of Ne we take van der Waals' radius

Thus, (a)

62. A-19 s-block

B-22 d-block

C-32 p-block

D-64 f-block

Thus, (b)

63. (c) 64. (d) 65. (a)

66. (a) K(19)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$  $K^+(19) 1s^2 2s^2 2p^6 3s^2 3p^6$ 

colourless being no unpaired electron in d-orbital

Thus, (a) is incorrect.

(b) Na(11)  $1s^2 2s^2 2p^6 3s^1$  s-block — true(c) Cu(29)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$  s-block — true(d) Cr(24)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ 

|                      |                      |                      |  |  |
|----------------------|----------------------|----------------------|--|--|
| $\uparrow\downarrow$ | $\uparrow\downarrow$ | $\uparrow\downarrow$ |  |  |
|----------------------|----------------------|----------------------|--|--|

Hund's rule absent

Thus, (d) is true

Only (a) is incorrect.

67.  $Cu^+$  is colourless $Sc^{3+}$  is colourless $Na^+, Mg^{2+}, Al^{3+}$  — colourless

as they have no electron unpaired in d-orbitals.

Thus, (b)

68. Crystal &gt; van der Waals' &gt; covalent

Thus, (a)

69. p-block element of higher periods

Ge, Sn, Pb

Thus, (c)

70. Gd(64)  $4f^7 5d^1$ 

eight unpaired electron

$$\text{Sum of spin} = 8 \times \frac{1}{2} = 4$$

Thus, (d)

71. U n q

 $\downarrow \downarrow \downarrow$ 

1 0 4

Thus, (c)

72. Size of cation decides lattice energy and thermal stability.

Smaller size, larger polarising power thus larger the lattice energy.

Thus,  $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl} > \text{CsCl}$

Thus, (b)

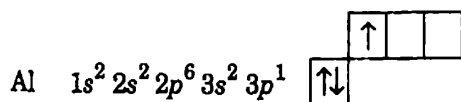
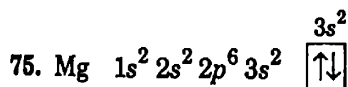
| 73.              | Z  | electron |
|------------------|----|----------|
| $\text{K}^+$     | 19 | 18       |
| $\text{S}^{2-}$  | 16 | 18       |
| $\text{Cl}^-$    | 17 | 18       |
| $\text{Ca}^{2+}$ | 20 | 18       |

Above are isoelectronic species, hence size  $\propto \frac{1}{Z}$

Thus,  $\text{S}^{2-} > \text{Cl}^- > \text{K}^+ > \text{Ca}^{2+}$

Thus, (c)

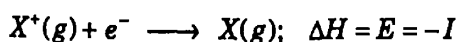
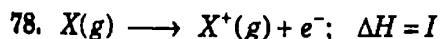
74. (d)



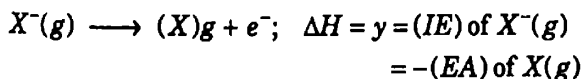
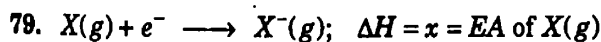
Thus, (c)

76. (c)  $\text{NH}_4^+$  is from non-metal N

77. (a)



Thus, (b)



Thus, (a), (b), (c) are true

Thus, (d)

80. (c) 81. (a) 82. (b)

83. Smaller size, larger charge  $\Rightarrow$  larger hydration and hydration energy

Size  $\text{Ca}^{2+} < \text{Si}^{2+} < \text{Ba}^{2+}$

hydration  $\text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$

Thus, (a)

84. Unpaired electrons = N

$$\text{Magnetic moment} = \sqrt{N(N+2)} \text{ BM}$$

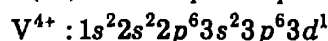
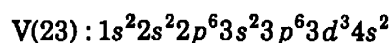
$$\sqrt{N(N+2)} = 1.73$$

$$N(N+2) = (1.73)^2 = 3$$

$$N^2 + 2N - 3 = 0$$

$$(N+3)(N-1) = 0$$

Thus,  $N = 1$  (one unpaired electron)



Thus,  $\text{VCl}_4$

Thus, (c)

85.  $\text{Ni}^{2+}$  is smallest thus, (a)

86.  $(IE)_1$  of Be > B

Thus, (b) is incorrect

87. Size  $\propto \frac{1}{Z}$  for isoelectronic ion.

Thus,  $\text{O}^{2-} > \text{F}^- > \text{Na}^+ > \text{Al}^{3+}$

(Z) 8 9 11 13

Thus, (d)

81.  $r_n = \frac{n^2 a_0}{Z^*}$

$$r_n \propto \frac{1}{Z^*}$$

Thus, (a)

89. (d)

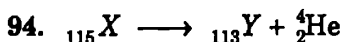
90. Size  $\propto \frac{1}{Z}$  for isoelectronic ion

Size :  $\text{C}^{4-} > \text{N}^{3-} > \text{O}^{2-} > \text{F}^-$

Z : 6 7 8 9

Thus, (a)

91. (b) 92. (c) 93. (d)

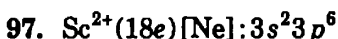


Thus, (a)

95. (d)

96.  $(n-1)d^5 ns^1$  represents group VIB (transition metals) of d-block

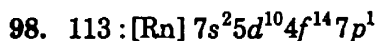
Thus, (d)



$\text{Sc}[\text{Ne}] : 3s^2 3p^6 4s^2 3d^1$  Thus, d-block IIIB group

Thus, given matching is incorrect.

Thus, (a)



Thus, p-block element

Thus, (b)

99. Valence electrons in  $M(113) = 3$

Thus,  $M^{3+}$  is the stable cation but due to inert pair effect  $M^+$  is most stable

Thus, (c)



Valence shell is  $7s^2 7p^3$  with five electrons.

Thus, +5, +3 are variable oxidation state. But due to inert-pair effects  $M^{5+} < M^{3+}$  (stable).

Thus, (a)

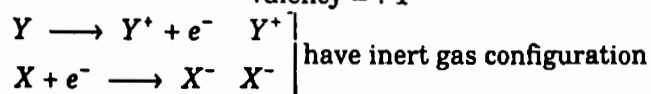
101. (a)

102.  $X : ns^2 np^5$  electronegative element

valency = -1

 $Y$  : electropositive alkali metal

valency = +1

Compound is  $YX$ 

Thus, (d)

103. (b)

104. Oxygen family is chalcogens.

Thus, (d)

105.  $M^{3+} : [Ar] 3d^{10}$  $M : [Ar] 3d^{10} 4s^1 4p^1$ Thus,  $p$ -block

Thus, (b)

106. (c) 107. (d)

108. Alkali (Li, Na, K) and alkaline earth metals (Ca, Sr, Ba) impart colour in flame

Thus, (b)

109. (c)

110.  $Fe : [Ar] 3d^6 4s^2$  $Fe^{2+} : [Ar] 3d^6$ 

Thus, (b)

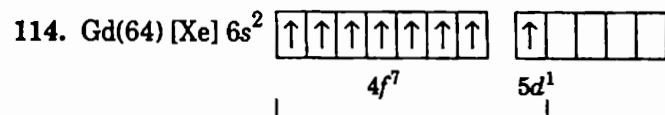
111. (b)

112. Lanthanides are  $f$ -block elements.

Thus, (d)

113. Actinides and lanthanides constitute  $f$ -blocks

Thus, (b)



all electrons, unpaired, hence stable

Thus, (a)

115. 1 1 5

$$\begin{array}{ccc} \uparrow & \uparrow & \uparrow \\ U & u & p \end{array}$$

Thus, (c)

116. (a) 117. (b)

118.  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$  : it is a case of alkali metals (K).

Thus, graded properties will be shown by element with identical configuration of the valence shell.

Thus, (c)

119. (a)

120. Element (113) lies below Tl (group 13, i.e., IIIA)

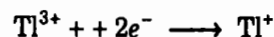
Thus, it resembles Ga

Thus, (b)

121. Due to inert-pair effect

Stability of  $Al^{3+} < Sb^{3+} < Bi^{3+}$ 

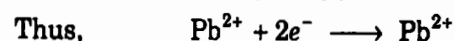
Thus, (c)

122. Stability of  $Ga^+ > In^+ > Tl^+$ and  $Ga^+ < In^{3+} < Tl^{3+}$ and  $Tl^+ > Tl^{3+}$ Thus,  $Tl^{3+}$  salts are easily reduced to  $Tl^+$ . Most spontaneous reaction is

Thus, (c)

| 123. | Element  | Compound with oxygen | Valency |
|------|----------|----------------------|---------|
|      | Halogen  | : $Cl_2O_7$          | +7      |
|      | Oxygen   | : $O_3$              | 0       |
|      | Nitrogen | : $N_2O_5$           | +5      |
|      | Boron    | : $B_2O_3$           | +3      |

Thus, (a)

124. Stability of  $Pb^{2+} > Sn^{2+} > Ge^{2+}$  $Pb^{4+} < Sn^{4+} < Ge^{4+}$  $Pb^{2+} > Pb^{4+}$  $Sn^{4+} > Sn^{2+}$  $Ge^{4+} > Ge^{2+}$ Thus,  $Pb^{4+}$  salts are better oxidising agent being easily reduced to  $Pb^{2+}$ .

Thus, (b)

125. Valence electrons in  $A = 3$ Valence electrons in  $B = 6$ Thus  $A$  is electropositive and  $B$  is electronegative;  $A$  can lose three electrons and  $B$  can gain two electrons to attain stable configuration.Thus,  $A$  exists as  $A^{3+}$ and  $B$  as  $B^{2-}$ Thus, compound is  $A_2B_3$ 

Thus, (d)

126. (a)

127.  $He^+$ ,  $Li^{2+}$  and  $Be^{3+}$  each has one electron, hence no screening.

Thus, (d)

128. Effective nuclear charge  $Z_{eff} = Z - S$ where  $Z$  = atomic numberand  $S$  = screening constant= 0.35 per electron for electron in  $n$ th orbit.= 0.85 per electron for electrons in  $(n-1)$ th orbit

= 1.00 per electron for electrons in

 $(n-2)$ th,  $(n-3)$ th,  $(n-4)$ th orbit= 0.30 per electron in  $1s$ -orbital (when alone)

Be  $1s^2 2s^2$  one valence-electron in  $2s$  is screened by one electron in  $2s$ -orbital ( $n$ th orbit) and two electrons in  $1s$  orbital ( $(n-1)$ th orbit)

$$\therefore S = 0.35 + 2 \times 0.85 = 2.05$$

$$\therefore Z_{\text{eff}} = 4 - 2.05 = 1.95 \text{ (given)}$$

Be<sup>+</sup>  $1s^2 2s^1$   $2s$ -electron is screened by two electrons in  $1s$ -orbital ( $(n-1)$ th orbit)

$$S = 2 \times 0.85 = 1.70$$

$$\therefore Z_{\text{eff}} = 4 - 1.70 = 2.30$$

Be<sup>2+</sup>  $1s^2$  one electron in  $1s$ -orbital (alone exists) is screened by another electron in same orbit. Thus,

$$S = 0.30$$

$$\therefore Z_{\text{eff}} = 4 - 0.30 = 3.70$$

Be<sup>3+</sup>  $1s^1$  no-screening (single electron)

Thus,  $Z_{\text{eff}} = 4$ .

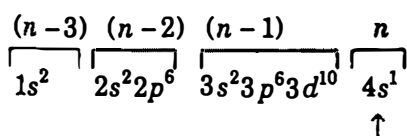
Thus,  $Z_{\text{effective}} : \text{Be} < \text{Be}^+ < \text{Be}^{2+} < \text{Be}^{3+}$

Thus, (a)

129. Refer question 128.

Thus, (a)

130. Cu(29)



This electron is screened by 18 electrons in  $(n-1)$ , 8-electrons in  $(n-2)$  and 2-electrons in  $(n-3)$

$$\text{Thus, } \sigma = \overbrace{8 \times 0.85}^{(n-1)s^2 p^6} + \overbrace{1 \times 10}^{(n-1)d^{10}} + \overbrace{8 \times 1}^{(n-2)d^{10}} + \overbrace{2 \times 1}^{(n-3)s^2} = 26.8$$

$$\text{Thus, } Z^* = 29 - 26.8 = 2.2$$

Thus, (a)

| 131.   | Atomic number (Z) | Period (n) |
|--------|-------------------|------------|
| (a) Cs | 55                | 6          |
| (b) Mg | 12                | 3          |
| (c) Ba | 56                | 6          |
| (d) Cr | 24                | 4          |

$$r_n \propto n^2, \text{ but in case of Cs and Ba, } r_n \propto \frac{1}{Z}$$

Thus, (a)

132. (a)

133.  $r_n \propto \frac{1}{Z}$  along a period.

Thus, B(5) > C(6) > N(7)

Thus, (b)

134. (c) 135. (c) 136. (b) 137. (c) 138. (d)

139. (c) 140. (a) 141. (b) 142. (a)

143. As electron is lost, effective nuclear charge increases, force of attraction increases. Hence,

$$(IE)_1 < (IE)_2 < (IE)_3$$

Thus, Mg<sup>2+</sup> has maximum (IE)

Thus, (c)

144. He  $\xrightarrow{I_1} \text{He}^+ \xrightarrow{I_2} \text{He}^{2+}$

$I_2 > I_1$ , hence, (d) is incorrect.

Thus, (d)

145. For alkali metals

$$(IE)_1 \ll (IE)_2$$

Thus, (c)

146. (c) 147. (c)

148. Along a group  $Z^*$  (effective nuclear charge) is almost constant. Thus, (IE) depends mainly on  $r_n$ .

Thus, (a)

149. (a) 150. (b)

### One or More Than One Options Correct

- (a), (b), (c), (d)
- (a), (b), (c)
- (a), (b), (c)
- (a), (c)
- (a), (b), (d)
- (b)
- (c)
- (d)
- (b)
- (a), (b), (d)

### Brain Twisters

- (a)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10} 7p^6 8s^2 5g^{18} 6f^{14} 7d^{10}$

(b)  $8s^2 7d^{10}, 7d^{10}$

(c) Four nodal planes, zero nodal sphere  
poor shielders, poor penetrators.

(d)  $Z^* = 4.35$

(e)  $\chi_{A-R} = 0.744 + [3590 \times (4.35 - 0.35)] / (150)^2$   
 $= 0.744 + 0.64 = 1.384$

The value should be much higher.

- $1.00 \text{ mg} = 1 \times 10^{-3} \text{ g} = \frac{1 \times 10^{-3}}{7} \text{ g mol Li}$

1 mol of Li is converted by = 520.3 kJ

$\therefore \frac{1 \times 10^{-3}}{7} \text{ mol is converted to Li}^+ \text{ by}$

$$= \frac{520 \times 1 \times 10^{-3}}{7} \text{ kJ}$$

$$= 0.0743 \text{ kJ}$$

- $(IE)_{\text{Total}} = (IE)_1 + \dots + (IE)_5$

$= 1.7058 \times 10^4 \text{ kJ mol}^{-1}$

$= 1.7058 \times 10^7 \text{ J mol}^{-1}$

Since,  $1.6 \times 10^{-19} \text{ J} = 1 \text{ eV}$

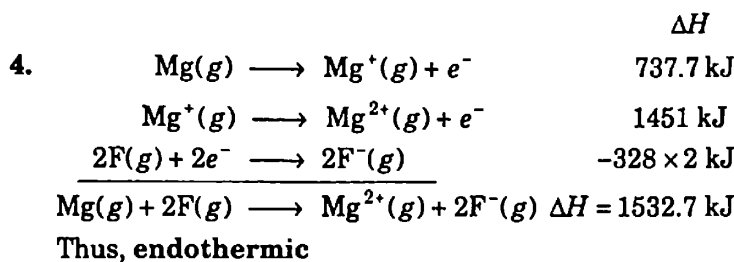
$$\therefore 1.7058 \times 10^7 \text{ J} = \frac{1.7058 \times 10^7}{1.6 \times 10^{-19}} \text{ eV mol}^{-1}$$

$$= 1.0661 \times 10^{26} \text{ eV mol}^{-1}$$



$$= \frac{1.0661 \times 10^{26}}{6.02 \times 10^{23}}$$

$$= 177.1 \text{ eV atom}^{-1}$$



5.  $1 \text{ eV atom}^{-1} = 1.6 \times 10^{-19} \text{ J atom}^{-1}$   
 $= 1.6 \times 10^{-19} \times 6.02 \times 10^{23} \text{ J mol}^{-1}$   
 $= 96.32 \times 10^3 \text{ J mol}^{-1}$   
 $= 96.32 \text{ kJ mol}^{-1}$

6.  $IE \text{ of F} = 27.91 \times 10^{-22} \text{ kJ atom}^{-1}$   
 $= 27.91 \times 10^{-22} \times 6.02 \times 10^{23} \text{ kJ mol}^{-1}$   
 $= 1680.2 \text{ kJ mol}^{-1}$   
 $IE \text{ of Cl} = 20.77 \times 10^{-22} \times 6.02 \times 10^{23} \text{ kJ mol}^{-1}$   
 $= 1250.35 \text{ kJ mol}^{-1}$   
 $EA \text{ of F} = -5.53 \times 10^{-22} \times 6.02 \times 10^{23} \text{ kJ mol}^{-1}$   
 $= -332.91 \text{ kJ mol}^{-1}$   
 $EA \text{ of Cl} = -5.78 \times 10^{-22} \times 6.02 \times 10^{23} \text{ kJ mol}^{-1}$   
 $= -347.96 \text{ kJ mol}^{-1}$

Let F =  $n_1$  moles and Cl =  $n_2$  moles

For the formation of cation

$$1680.2n_1 + 1250.35n_2 = 284$$

or  $n_1 + 0.744n_2 = 0.1690 \quad \dots(i)$

and for the formation of anion

$$332.91n_1 + 347.96n_2 = 68.8$$

or,  $n_1 + 1.045n_2 = 0.207 \quad \dots(ii)$

From (i) and (ii)

$$n_1 = 0.0785 \text{ mol}$$

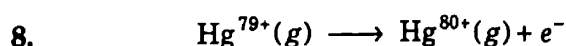
$$n_2 = 0.123 \text{ mol}$$

$$\text{Total moles} = 0.123 + 0.0785 = 0.2015$$

$$\therefore \text{Mol \% of F} = \frac{0.123}{0.2015} \times 100 = 61.04\%$$

$$\text{Mol \% F} = 38.96\%$$

7.  $(IE)_{\text{He}^+} = (-E_n)$   
 $= \frac{2.18 \times 10^{-18} Z^2}{n^2} \text{ J atom}^{-1}$   
 $= \frac{2.18 \times 10^{-18} \times (2)^2}{1} \text{ J atom}^{-1} \text{ for He}^+ (n=1, Z=2)$   
 $= 2.18 \times 10^{-18} \times 4 \times 6.02 \times 10^{23} \text{ J mol}^{-1}$   
 $= 5.2494 \times 10^6 \text{ J mol}^{-1}$   
 $= 5.2494 \times 10^3 \text{ kJ mol}^{-1}$



$\text{Hg}^{79+}(g)$  is isoelectronic of hydrogen (electron = 1)  
 $(Z = 79, n = 1)$

From Q. 7.

$$\therefore (IE)_{\text{Hg}^{79+}} = \frac{2.18 \times 10^{-18} \times (79)^2}{1} \text{ J atom}^{-1}$$

$$= 1.36 \times 10^{-17} \text{ J atom}^{-1}$$

$$= \frac{2.18 \times 10^{-18} \times (79)^2 \times 6.02 \times 10^{23}}{1000} \text{ kJ mol}^{-1}$$

$$= 8.19 \times 10^6 \text{ kJ mol}^{-1}$$

9. Volume of K atom =  $\frac{4}{3} \pi r^3 = \frac{4}{3} \pi (216)^3$   
 Volume of  $\text{K}^+$  ion =  $\frac{4}{3} \pi (133)^3$   
 Decrease in volume =  $\frac{4}{3} \pi [(216)^3 - (133)^3]$   
 $\% \text{ decrease} = \frac{\frac{4}{3} \pi [(216)^3 - (133)^3]}{\frac{4}{3} \pi (216)^3} \times 100$   
 $= 76.66\%$

## Passage Comprehension Questions

### Passage 1

1. (a) 2. (b) 3. (d)

### Passage 2

1. (b) 2. (a) 3. (c) 4. (b)

### Passage 3

1. (c) 2. (c) 3. (a)

### Passage 4

1. (c) 2. (a) 3. (c)

### Passage 5

1. (b) 2. (d) 3. (a) 4. (c)

### Passage 6

1. (d) 2. (c) 3. (b)

### Passage 7

1. (a), (b), (c), (d) 2. (a)

### Passage 8

1. (a) 2. (b) 3. (c) 4. (c)

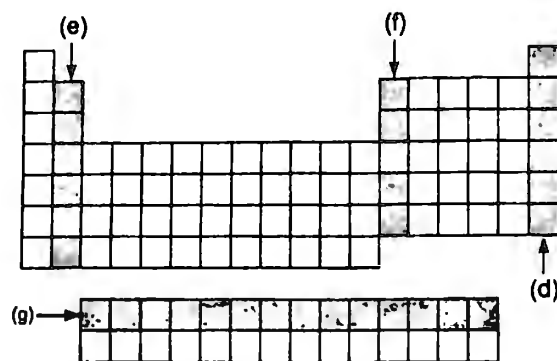
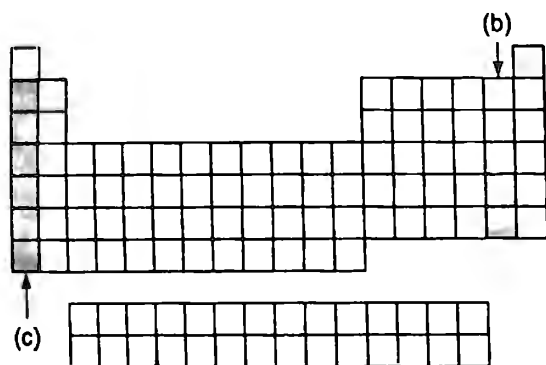
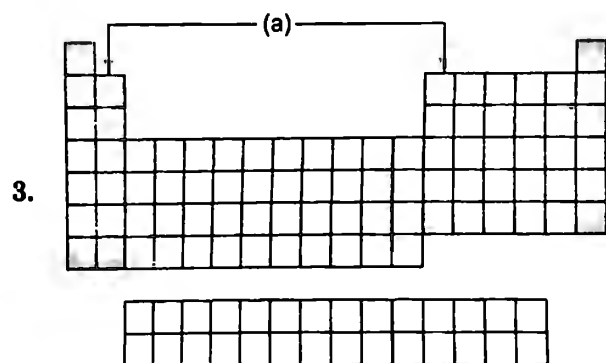
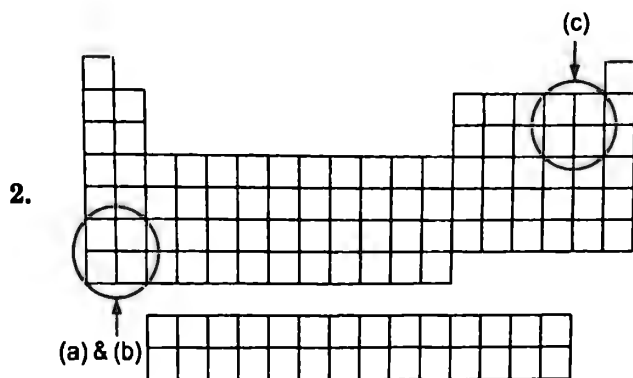
## Assertion & Reason

1. (b) 2. (a) 3. (c) 4. (b) 5. (b) 6. (a)  
 7. (a) 8. (b) 9. (a) 10. (b)

## True & False

1. T : Due to shielding effect  
 2. T :  $2\text{NaOH} + \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \longrightarrow 2\text{Na}[\text{Al}(\text{OH})_4]$   
 3. F : Neutral oxide  
 4. F  $\text{PbO}_2$  (oxidation number of Pb = +4) is an oxidising agent since  $\text{Pb}^{2+}$  is more stable than  $\text{Pb}^{4+}$  due to inert pair effect.  
 $\text{Pb}^{4+} + 2e^- \longrightarrow \text{Pb}^{2+}$





4. (a) A :  $\text{CaO}$ , B :  $\text{Al}_2\text{O}_3$ , C :  $\text{SO}_3$ , D :  $\text{SeO}_3$   
 (b) basic :  $\text{CaO}$  (c) most ionic :  $\text{CaO}$   
 acidic :  $\text{SO}_3, \text{SeO}_3$  most covalent :  $\text{SO}_3$   
 amphoteric;  $\text{Al}_2\text{O}_3$   
 (d)  $\text{CaO}, \text{Al}_2\text{O}_3$  : three-dimensional structure  
 $\text{SO}_3, \text{SeO}_3$  : molecular  
 (e)  $\text{CaO}$  : highest melting point  
 $\text{SO}_3$  : lowest melting point
5. (a) A :  $\text{NaH}$  (b) ionic (c)  $\text{Na} = +1, \text{H} = -1$   
 B :  $\text{PdH}_x$  interstitial  
 C :  $\text{H}_2\text{S}$  covalent S = -2, H = +1  
 D :  $\text{HI}$  covalent I = -1, H = +1

# Oxidation-Reduction

**A fair business of gain of electrons (reduction) and loss of electrons (oxidation) is a redox reaction. How much is lost in a half-reaction, is also gained in equal amount (electrons) — actually the best fair deal.**

## Quick Points

- Number of ionisable H atoms (attached to electronegative atom O) determines basicity of an acid.  
 $\text{HNO}_3, \text{H}_3\text{PO}_2$  (monobasic acid) — one H attached to O-atom  
 $\text{H}_2\text{SO}_4, \text{H}_3\text{PO}_3$  (dibasic acid) — two H attached to O-atoms  
 $\text{H}_3\text{PO}_4$  (tribasic acid) — three H attached to O-atoms
- Superoxide ion is  $\text{O}_2^-$
- Peroxide ion is  $\text{O}_2^{2-}$
- Mole =  $\frac{\text{mass}}{\text{molar mass}}$
- $N_0$  (Avogadro's number) =  $6.02 \times 10^{23} \text{ mol}^{-1}$
- $\Delta G^\circ = -nFE^\circ$   
 where,  $n$  = number of electrons exchanged  
 $F$  = number of faradays  
 $E^\circ$  = standard electrode potential  
 $\Delta G^\circ$  = standard Gibb's free energy change
- If different number of electrons are exchanged in a series of reactions then

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

or

$$E_3^\circ = \frac{n_1 E_1^\circ + n_2 E_2^\circ}{n_3}$$

$$E = E^\circ - \frac{0.0591}{n} \log Q$$

where,  $Q$  = reaction quotient.

$$E^\circ = \frac{2.303RT}{nF} \log K_{\text{eq}}$$

at equilibrium when  $E = 0$

and  $Q$  = equilibrium constant =  $K_{\text{eq}}$

## Learning Framework of the Chapter

- Oxidation Number and Oxidation State
- Oxidation and Reduction
- How to Balance a Redox Reaction
- Balanced Redox Reactions
- Equivalent Weights

## Oxidation Number and the Oxidation State

The oxidation number (O.N.) of an atom in a molecule or in a polyatom ion is a hypothetical charge the atom would have if the electrons in each bond were located on the more electronegative atom.

The oxidation number (or oxidation state) of an element in a compound is determined as the number of electrons that have passed from one atom of a given element to other atoms (positive oxidation) or to one atom of a given element from other atom (negative oxidation). Oxidation states simplify the whole process of working out what is being oxidised and what is being reduced in redox reactions.

- Oxidation state is the oxidation number per atom.
- An unreacted element has oxidation number of zero.
- A monoatomic ion has oxidation number equal to its charge.

### Oxidation Number of Elements in Covalent Compounds and in Ions

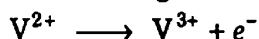
| Element/ion    | O.N. | Element/ion                  | O.N.            |
|----------------|------|------------------------------|-----------------|
| H <sub>2</sub> | 0    | Mg <sup>2+</sup>             | +2              |
| O <sub>2</sub> | 0    | Fe <sup>3+</sup>             | +3              |
| N <sub>2</sub> | 0    | Mn <sup>7+</sup>             | +7              |
| Na             | 0    | O <sub>2</sub> <sup>-</sup>  | -0.5 (per atom) |
| Mg             | 0    | O <sup>2-</sup>              | -2              |
| H <sup>+</sup> | +1   | O <sub>2</sub> <sup>2-</sup> | -1 (per atom)   |
| H <sup>-</sup> | -1   |                              |                 |

Vanadium forms a number of different ions — for example, V<sup>2+</sup> and V<sup>3+</sup>. If you think about how these might be produced from vanadium metal, the 2+ ion will be formed by oxidising the metal by removing two electrons:



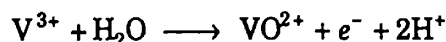
The vanadium is now said to be in an oxidation state of +2.

Removal of another electron gives the V<sup>3+</sup> ion



The vanadium now has an oxidation state of +3.

Removal of another electron gives a more unusual looking ion, VO<sup>2+</sup>.



The vanadium is now in an oxidation state of +4. Notice that the oxidation state isn't simply counting the charge on the ion (that was true for the first two cases but not for this one).

The positive oxidation state is counting the total number of electrons which have had to be removed-starting from the element.

It is also possible to remove a fifth electron to give another ion (easily confused with the one before). The oxidation state of the vanadium is now +5.

Every time you oxidise the vanadium by removing another electron from it, its oxidation state increases by 1.

Fairly obviously, if you start adding electrons again the oxidation state will fall. You could eventually get back to the element vanadium which would have an oxidation state of zero.

What if you kept on adding electrons to the element? You can't actually do that with vanadium, but you can with an element like sulphur.

Oxidation states are represented by integers, which can be positive, zero, or negative. In some cases average oxidation state of element is a fraction such as 8/3 for iron in magnetite.

### Working Out the Oxidation States

You don't work out oxidation states by counting the numbers of electrons transferred. It would take far too long. Instead you learn some simple rules, and do some very simple sums.

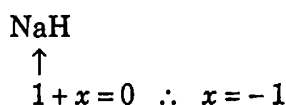
- The oxidation state of an uncombined element is zero. That's obviously so, because it hasn't been either oxidised or reduced yet. This applies whatever the structure of the element-whether it is, for example Xe or Cl<sub>2</sub> or S<sub>8</sub>, or whether it has a giant structure like carbon or silicon.
- The sum of the oxidation states of all the atoms or ions in a neutral compound is zero.
- The sum of the oxidation states of all the atoms in an ion is equal to the charge on the ion.
- The more electronegative element in a substance is given a negative oxidation state. The less electronegative one is given a positive oxidation state. **Remember that fluorine is the most electronegative element with oxygen second.**
- Some elements almost always have the same oxidation states in their compounds

| Element        | Usual oxidation state | Exceptions                               |
|----------------|-----------------------|------------------------------------------|
| Group 1 metals | always +1             |                                          |
| Group 2 metals | always +2             |                                          |
| Oxygen         | usually -2            | except in peroxides and F <sub>2</sub> O |
| Hydrogen       | usually +1            | except in metal hydrides where it is -1  |
| Fluorine       | always -1             |                                          |
| Chlorine       | usually -1            | except in compounds with O or F          |

### The reasons for the exceptions

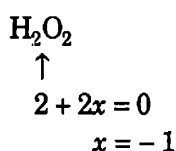
- (i) *Hydrogen in the metal hydrides* Metal hydrides include compounds like sodium hydride, NaH. In this, the hydrogen is present as a hydride ion, H<sup>-</sup>. The oxidation state of a simple ion like hydride is equal to the charge on the ion-in this case, -1.

Alternatively, you can think of it that the sum of the oxidation states in a neutral compound is zero. Since Group 1 metals always have an oxidation state of +1 in their compounds, it follows that the hydrogen must have an oxidation state of -1 (+1 - 1 = 0).



(ii) *Oxygen in peroxides* Peroxides include hydrogen peroxide,  $\text{H}_2\text{O}_2$ . This is an electrically neutral compound and so the sum of the oxidation states of the hydrogen and oxygen must be zero.

Since, each hydrogen has an oxidation state of +1, each oxygen must have an oxidation state of -1 to balance it.



(iii) *Oxygen in  $\text{F}_2\text{O}$*  The problem here is that oxygen isn't the most electronegative element. The fluorine is more electronegative and has an oxidation state of -1. In this case, the oxygen has an oxidation state of +2.

(iv) *Chlorine in compounds with fluorine or oxygen* There are so many different oxidation states that chlorine can have in these, that it is safer to simply remember that the chlorine doesn't have an oxidation state of -1 in them, and work out its actual oxidation state when you need it. You will find an example of this below.

- While naming the ion or compound, it is desirable to **put oxidation number per atom** (i.e., oxidation state) in Roman figures within brackets (anion end with ate) (Table 4.1).

Table 4.1 Naming the Acid and its Ions

| Oxoanions             | Formula                     | Acids              | Formula                          |
|-----------------------|-----------------------------|--------------------|----------------------------------|
| Bromate (I)           | $\text{BrO}^-$              | Bromic (I)         | $\text{HBrO}$                    |
| Bromate (III)         | $\text{BrO}_2^-$            | Bromic (III)       | $\text{HBrO}_2$                  |
| Bromate (V)           | $\text{BrO}_3^-$            | Bromic (V)         | $\text{HBrO}_3$                  |
| Bromate (VII)         | $\text{BrO}_4^-$            | Bromic (VII)       | $\text{HBrO}_4$                  |
| Chromate (VI)         | $\text{CrO}_4^{2-}$         | Chromic (VI)       | $\text{H}_2\text{CrO}_4$         |
| Nitrate (V)           | $\text{NO}_3^-$             | Nitric             | $\text{HNO}_3$                   |
| Nitrate (III)         | $\text{NO}_2^-$             | Nitrous            | $\text{HNO}_2$                   |
| Phosphate (V)         | $\text{PO}_4^{3-}$          | Phosphoric         | $\text{H}_3\text{PO}_4$          |
| Sulphate (IV)         | $\text{SO}_3^{2-}$          | Sulphurous         | $\text{H}_2\text{SO}_3$          |
| Sulphate (VI)         | $\text{SO}_4^{2-}$          | Sulphuric          | $\text{H}_2\text{SO}_4$          |
| Peroxodisulphate (VI) | $\text{S}_2\text{O}_8^{2-}$ | Peroxy-disulphuric | $\text{H}_2\text{S}_2\text{O}_8$ |

## Elements with Multiple Oxidation States

Most elements have more than one possible oxidation state. Carbon has nine integer oxidation states, and there are also molecules in which the average degree of oxidation of several carbons is fractional.

### Integer oxidation states of carbon with examples

1. -4 :  $\text{CH}_4$
2. -3 :  $\text{C}_2\text{H}_6$
3. -2 :  $\text{CH}_3\text{Cl}$
4. -1 :  $\text{C}_2\text{H}_2$
5. 0 :  $\text{CH}_2\text{Cl}_2$
6. +1 :  $\text{CHCl}_2\text{—CHCl}_2$
7. +2 :  $\text{CHCl}_3$
8. +3 :  $\text{C}_2\text{Cl}_6$
9. +4 :  $\text{CCl}_4$

### Examples of fractional oxidation states for carbon

1. - (6/5) :  $\text{C}_5\text{H}_5^-$
2. - (6/7) :  $\text{C}_7\text{H}_7^+$
3. - (10/8) :  $\text{C}_8\text{H}_8^{2-}$

### Oxygen has 8 different oxidation states

1. -2 in oxides, e.g.,  $\text{ZnO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$
2. -1 in peroxides, e.g.,  $\text{H}_2\text{O}_2$
3. - (1/2) in superoxides, e.g.,  $\text{KO}_2$
4. - (1/3) in inorganic ozonides, e.g.,  $\text{RbO}_3$
5. 0 in  $\text{O}_2$
6. + (1/2) in dioxygenyl, e.g., dioxygenyl hexfluoroarsenate  $\text{O}_2^+[\text{AsF}_6]^-$
7. +1 in  $\text{O}_2\text{F}_2$
8. +2 in  $\text{OF}_2$

Note that since fluorine is more electronegative than oxygen,  $\text{O}_2\text{F}_2$  and  $\text{OF}_2$  are considered as fluorides, rather than as a peroxide and an oxide.

## Fractional Oxidation States

Fractional oxidation states are often used to represent the average oxidation states of several atoms in a structure. For example, in  $\text{KO}_2$ , the superoxide ion has a charge of -1 divided among two equivalent atoms, so each oxygen is assigned an oxidation state of -1/2. This ion is described as a resonance hybrid of two Lewis structures, and each oxygen has oxidation state 0 in one structure and -1 in the other.

For the cyclopentadienyl ion  $\text{C}_5\text{H}_5^-$ , the oxidation state of C is  $(-1) + (-1/5) = -6/5$ . The -1 occurs because each C is bonded to one less electronegative H, and the -1/5 because the total ionic charge is divided among five equivalent C.

If the average refers to atoms which are not equivalent, the average oxidation state may not be

representative of each atom. This is true in magnetic  $\text{Fe}_3\text{O}_4$  whose formula leads to an average oxidation state of  $+8/3$ . In fact **two thirds of the iron ions are  $\text{Fe}^{3+}$  and one third  $\text{Fe}^{2+}$ .**

Similarly the ozonide ion  $\text{O}_3^-$  has an average oxidation state of  $-1/3$ . This ion is V-shaped with a central oxygen which is not equivalent to the two others and cannot be assumed to have the same oxidation state.

You will have come across names like iron (II) sulphate and iron (III) chloride. The (II) and (III) are the oxidation states of the iron in the two compounds:  $+2$  and  $+3$  respectively. That tells you that they contain  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions.

This can also be extended to the negative ion. Iron (II) sulphate is  $\text{FeSO}_4$ . There is also a compound  $\text{FeSO}_3$  with the old name of iron (II) sulphite. The modern names reflect the oxidation states of the sulphur in the two compounds.

The sulphate ion is  $\text{SO}_4^{2-}$ . The oxidation state of the sulphur is  $+6$ . The ion is more properly called the sulphate (VI) ion.

The sulphite ion is  $\text{SO}_3^{2-}$ . The oxidation state of the sulphur is  $+4$ . This ion is more properly called the sulphate(IV) ion. **The ate ending simply shows that the sulphur is in a negative ion.**

So,  $\text{FeSO}_4$  is properly called iron (II) sulphate(VI), and  $\text{FeSO}_3$  is iron(II) sulphate (IV). In fact, because of the easy confusion between these names, the old names sulphate and sulphite are normally still used in introductory chemistry courses.

**Oxidation numbers of underlined atoms have been determined by known values of the O.N. of other atoms in it.**

$$(1) (a) \text{Cr}\underline{\text{O}_4}^{2-} \quad x - 8 = -2 \quad x = 6$$

$$(b) \underline{\text{Cr}_2}\text{O}_7^{2-} \quad 2x - 14 = -2, \quad 2x = 12$$

or  $x = 6$  (per atom)

$$(2) (a) \text{H}_3\underline{\text{P}}\text{O}_4 \quad 3 + x - 8 = 0, \quad x = +5$$

$$(b) \text{H}_3\underline{\text{P}}\text{O}_3 \quad 3 + x - 6 = 0, \quad x = +3$$

$$(c) \text{H}_3\underline{\text{P}}\text{O}_2 \quad 3 + x - 4 = 0, \quad x = +1$$

$$(3) (a) \text{H}_2\underline{\text{S}}\text{O}_3 \quad 2 + x - 6 = 0 \quad x = +4$$

$$(b) \text{H}_2\underline{\text{S}}\text{O}_4 \quad 2 + x - 8 = 0 \quad x = +6$$

$$(c) \text{H}_2\underline{\text{S}_2}\text{O}_3 \quad 2 + 2x - 6 = 0 \quad x = +2$$

$$(4) (a) \text{H}\underline{\text{Cl}}\text{O}_4 \quad 1 + x - 8 = 0 \quad x = +7$$

$$(b) \text{H}\underline{\text{Cl}}\text{O}_3 \quad 1 + x - 6 = 0 \quad x = +5$$

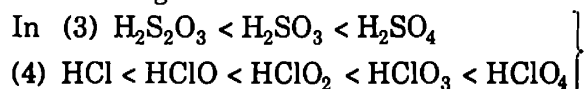
$$(c) \text{H}\underline{\text{Cl}}\text{O}_2 \quad 1 + x - 4 = 0 \quad x = +3$$

$$(d) \text{H}\underline{\text{Cl}}\text{O} \quad 1 + x - 2 = 0 \quad x = +1$$

$$(e) \text{H}\underline{\text{Cl}} \quad 1 + x = 0 \quad x = -1$$

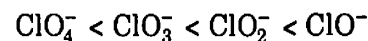
— In (2), (3) and (4) oxyacids have atoms with different O.N.

— **Greater the O.N. of the element forming oxyacids, greater the acid strength except for oxyacids of phosphorus :** Thus, acid strength increases.



order of acid strength

If acid is strong its conjugate base (formed when  $\text{H}^+$  is lost from an acid) is weak and *vice-versa*. Thus, basic strength of conjugate bases of oxyacids of Cl will be in order:



**Hence, greater the O.N. of the element in conjugate bases, smaller the basic strength.**

Table 4.2 gives oxidation number of underlined atom.

**Table 4.2 Oxidation Number of the Atom in Different Species (Ion/Molecule)**

|                                                        |                 |                                                 |                                                                                                              |
|--------------------------------------------------------|-----------------|-------------------------------------------------|--------------------------------------------------------------------------------------------------------------|
| $[\underline{\text{Ni}}(\text{CN})_4]^{2-}$            | +2              | $\text{H}\underline{\text{N}}\text{O}_2$        | +3                                                                                                           |
| $\underline{\text{Ni}}(\text{CO})_4$                   | 0               | $\text{H}\underline{\text{N}}\text{O}_3$        | +5                                                                                                           |
| $[\underline{\text{Fe}}(\text{H}_2\text{O})]^{2+}$     | +2              | $\text{H}_2\underline{\text{N}}_2\text{O}_2$    | +1                                                                                                           |
| $\underline{\text{Mn}}\text{O}_4^-$                    | +7              | $\underline{\text{C}}_6\text{H}_{12}\text{O}_6$ | 0                                                                                                            |
| $\underline{\text{Mn}}\text{O}_4^{2-}$                 | +6              | $\underline{\text{C}}\text{O}_2$                | +4                                                                                                           |
| $\underline{\text{Mn}}\text{O}_2$                      | +4              | $\underline{\text{N}}\text{H}_3$                | -3                                                                                                           |
| $\underline{\text{N}}\text{O}_2$                       | +4              | $\underline{\text{N}}_2\text{H}_4$              | -2                                                                                                           |
| $\text{NH}_2\text{OH}$                                 | -1              | $\underline{\text{N}}_2\text{O}$                | +1                                                                                                           |
| $\underline{\text{N}}\text{O}$                         | +2              |                                                 |                                                                                                              |
| $\underline{\text{N}}_2\text{O}_5$                     | +5 (per atom)   |                                                 |                                                                                                              |
| $\underline{\text{N}}_2\text{O}_3$                     | +3 (per atom)   |                                                 |                                                                                                              |
| $\underline{\text{K}}\text{O}_2$                       | -0.5 (per atom) |                                                 |                                                                                                              |
| $\underline{\text{Cr}}\text{O}_5$                      | +6              |                                                 |                                                                                                              |
|                                                        |                 |                                                 | It has two peroxy linkages<br>$\text{CrO}(\text{O}_2)_2$                                                     |
| $\text{H}_2\underline{\text{S}}\text{O}_5$             | +6              |                                                 | It has one peroxy linkage<br>                                                                                |
| $\text{H}_2\underline{\text{S}_2}\text{O}_8$           | +6 (per atom)   |                                                 | It has one peroxy linkage                                                                                    |
| $[\underline{\text{Fe}}(\text{CN})_6]^{4-}$            | +2              |                                                 |                                                                                                              |
| $[\underline{\text{Fe}}(\text{CN})_6]^{3-}$            | +3              |                                                 |                                                                                                              |
| $[\underline{\text{Fe}}(\text{CN})_5(\text{NO})]^{2-}$ | +2              |                                                 |                                                                                                              |
| $\underline{\text{P}}\text{OCl}_3$                     | +5              |                                                 | O as well as Cl are attached to P directly hence ON of O = -2, and that of Cl = -1                           |
| $\underline{\text{P}}\text{OCl}_3$                     | -2              |                                                 |                                                                                                              |
| $\text{PO}\underline{\text{Cl}}_3$                     | -1 (per atom)   |                                                 |                                                                                                              |
| $[\underline{\text{Cr}}(\text{en})_3]^{3+}$            | +3              |                                                 | $\text{en} = \begin{pmatrix} \text{CH}_2\text{NH}_2 \\   \\ \text{CH}_2\text{NH}_2 \end{pmatrix}$ is neutral |

Table 4.3 gives common oxidation numbers for group A elements.

**Table 4.3 Common Oxidation Number (States) for Group A Elements in Compounds and Ions**

| Element (s)                   | Common O.N.                                                                                            | Examples                                                                                                                                                      | Other O.N.                                                                                                                                                                                                                                                                                                                                                                                         |
|-------------------------------|--------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| H                             | +1                                                                                                     | H <sub>2</sub> O, CH <sub>4</sub> , NH <sub>4</sub> Cl                                                                                                        | -1 in metal hydrides, e.g., NaH, CaH <sub>2</sub>                                                                                                                                                                                                                                                                                                                                                  |
| Group IA                      | +1                                                                                                     | KCl, NaH, RbNO <sub>3</sub> , K <sub>2</sub> SO <sub>4</sub>                                                                                                  | None                                                                                                                                                                                                                                                                                                                                                                                               |
| Group IIA                     | +2                                                                                                     | CaCl <sub>2</sub> , MgH <sub>2</sub> , Ba(NO <sub>3</sub> ) <sub>2</sub> , SrSO <sub>4</sub>                                                                  | None                                                                                                                                                                                                                                                                                                                                                                                               |
| Group IIIA                    | +3                                                                                                     | AlCl <sub>3</sub> , BF <sub>3</sub> , Al(NO <sub>3</sub> ) <sub>3</sub> , GaI <sub>3</sub>                                                                    | None in common compounds                                                                                                                                                                                                                                                                                                                                                                           |
| Group IVA                     | +2<br>+4                                                                                               | CO, PbO, SnCl <sub>2</sub> , Pb(NO <sub>3</sub> ) <sub>2</sub> , CCl <sub>4</sub> , SiO <sub>2</sub> , SiO <sub>3</sub> <sup>2-</sup> , SnCl <sub>4</sub>     | Many others are also seen for C and Si                                                                                                                                                                                                                                                                                                                                                             |
| Group VA                      | -3 in binary compounds with metals<br>-3 in NH <sub>4</sub> <sup>+</sup> , binary compound s with H    | Mg <sub>3</sub> N <sub>2</sub> , Na <sub>3</sub> P, Ca <sub>3</sub> As<br>NH <sub>3</sub> , PH <sub>3</sub> , AsH <sub>3</sub> , NH <sub>4</sub> <sup>+</sup> | +3, e.g., NO <sub>2</sub> <sup>-</sup> , PCl <sub>3</sub> ,<br>+5, e.g., NO <sub>3</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , AsF <sub>5</sub> , P <sub>4</sub> O <sub>10</sub>                                                                                                                                                                                                          |
| Oxygen                        | -2                                                                                                     | H <sub>2</sub> O, P <sub>4</sub> O <sub>10</sub> , Fe <sub>2</sub> O <sub>3</sub> , CaO, ClO <sub>3</sub> <sup>-</sup>                                        | +2 in OF <sub>2</sub> , -1 in peroxides, e.g., H <sub>2</sub> O <sub>2</sub> , Na <sub>2</sub> O <sub>2</sub> , - $\frac{1}{2}$ in superoxides, e.g., KO <sub>2</sub> , RbO <sub>2</sub>                                                                                                                                                                                                           |
| Group VIA (other than oxygen) | -2 in binary compound s with metals and H<br>-2 in binary compound s with NH <sub>4</sub> <sup>+</sup> | H <sub>2</sub> S, CaS, Fe <sub>2</sub> S <sub>3</sub> , Na <sub>2</sub> Se, (NH <sub>4</sub> ) <sub>2</sub> S, (NH <sub>4</sub> ) <sub>2</sub> Se             | +4 with O and the lighter halogens, e.g., SO <sub>2</sub> , SeO <sub>2</sub> , Na <sub>2</sub> SO <sub>3</sub> , SO <sub>3</sub> <sup>2-</sup> , SF <sub>4</sub><br>+6 with O and the lighter halogens, e.g., SO <sub>3</sub> , TeO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> , SO <sub>4</sub> <sup>2-</sup> , SF <sub>6</sub>                                                                |
| Group VIIA                    | -1 in binary compound s with metals and H, -1 in binary compound s with NH <sub>4</sub> <sup>+</sup>   | MgF <sub>2</sub> , KI, ZnCl <sub>2</sub> , FeBr <sub>3</sub> , NH <sub>4</sub> Cl, NH <sub>4</sub> Br                                                         | Cl, Br, or I with O or with a lighter halogen<br>+1, e.g., BrF, ClO <sup>-</sup> , BrO <sup>-</sup> ;<br>+3, e.g., ICl <sub>3</sub> , ClO <sub>2</sub> <sup>-</sup> , BrO <sub>2</sub> <sup>-</sup> ;<br>+5, e.g., BrF <sub>5</sub> , ClO <sub>3</sub> <sup>-</sup> , BrO <sub>3</sub> <sup>-</sup> ;<br>+7, e.g., IF <sub>7</sub> , ClO <sub>4</sub> <sup>-</sup> , BrO <sub>4</sub> <sup>-</sup> |

Table 4.4 gives some non-zero oxidation numbers/ states.

### Do you know .....

By convention, oxidation numbers are represented as  $+n$  and  $-n$ , while ionic charges as  $n^+$  and  $n^-$ ; as  $+3$ , Fe<sup>3+</sup>,  $-3$ , X<sup>3-</sup> usually, the element with thze positive oxidation number is written first. ( $\overset{+1}{\text{Cl}}\overset{-2}{\text{O}}\overset{-1}{\text{O}}\overset{-1}{\text{O}}\overset{-1}{\text{O}}$ ), ( $\overset{+4}{\text{C}}\overset{-2}{\text{O}}\overset{-2}{\text{O}}$ )

However, for historic reasons, in compounds containing nitrogen and hydrogen, such as NH<sub>3</sub>, and many other compounds containing carbon and hydrogen, such as CH<sub>4</sub>, hydrogen is written last, although it has a positive oxidation state.

Most transition metals and the metals of Group IIIA (boron family), IVA (carbon family) and VA (nitrogen family), exhibit more than one oxidation number. These metals may form two or more binary compounds with the same non-metal. To distinguish among all possibilities, the oxidation number of the metal is indicated by a Roman numeral in parentheses following its name. This method can be applied to any binary compound of a metal and a non-metal, whether the compound is ionic or molecule. An older method still in use but not recommended by the IUPAC uses "ous" and "ic" suffixes to indicate lower and higher oxidation number respectively.

| Formula                         | Oxidation number of metal | IUPAC name            | Common name        |
|---------------------------------|---------------------------|-----------------------|--------------------|
| Cu <sub>2</sub> O               | +1                        | Copper (I) oxide      | Cuprous oxide      |
| CuF <sub>2</sub>                | +2                        | Copper (II) fluoride  | Cupric fluoride    |
| FeS                             | +2                        | Iron (II) sulphide    | Ferrous sulphide   |
| Fe <sub>2</sub> O <sub>3</sub>  | +3                        | Iron (III) oxide      | Ferric oxide       |
| SnCl <sub>2</sub>               | +2                        | Tin (II) chloride     | Stannous chloride  |
| SnCl <sub>4</sub>               | +4                        | Tin (IV) chloride     | Stannic chloride   |
| PbO                             | +2                        | Lead (II) oxide       | Plumbous oxide     |
| PbO <sub>2</sub>                | +4                        | Lead (IV) oxide       | Plumbic oxide      |
| Hg <sub>2</sub> Cl <sub>2</sub> | +1                        | Mercury (I) chloride  | Mercurous chloride |
| HgCl <sub>2</sub>               | +2                        | Mercury (II) chloride | Mercuric chloride  |

| Formula                        | Oxidation number | Name                       |
|--------------------------------|------------------|----------------------------|
| H <sub>2</sub> SO <sub>3</sub> | +4               | 2-units<br>Sulphurous acid |
| H <sub>2</sub> SO <sub>4</sub> | +6               |                            |
| HNO <sub>2</sub>               | +3               | 2-units<br>Nitrous acid    |
| HNO <sub>3</sub>               | +5               |                            |
| HBrO <sub>2</sub>              | +3               | 2-units<br>Bromous acid    |
| HBrO <sub>3</sub>              | +5               |                            |



**DEEP Focus**

Ternary acids that have one fewer O atoms than the “-ous” acids (two fewer O atoms than the “-ic” acids) are named using the prefix “hypo-” and the suffix “-ous”.

| Formula                                      | Oxidation number | Name                 |
|----------------------------------------------|------------------|----------------------|
| HClO                                         | +1               | hypochlorous acid    |
| H <sub>3</sub> PO <sub>2</sub>               | +1               | hypophosphorous acid |
| HIO                                          | +1               | hypoiodous acid      |
| H <sub>2</sub> N <sub>2</sub> O <sub>2</sub> | +1               | hyponitrous acid     |

**DEEP Focus**

Acids containing one more oxygen atom per central non-metal atom than the normal “-ic acid” are named “-per” acids.

| Formula           | Oxidation number | Name            |
|-------------------|------------------|-----------------|
| HClO <sub>4</sub> | +7               | perchloric acid |
| HBrO <sub>4</sub> | +7               | perbromic acid  |
| HIO <sub>4</sub>  | +7               | periodic acid   |

**Ternary acids (oxoacids)** are compounds of hydrogen, oxygen, and usually a non-metal. Non-metals that exhibit more than one oxidation state form more than one ternary acid. These ternary acids differ in the number of oxygen atoms they contain. The suffixes “-ous” and “-ic” indicate lower and higher oxidation states, respectively. The common ternary “-ic” acids are shown below.

Acids containing one fewer oxygen atom per central atom are named in the same way except that the “-ic” suffix is changed to “ous”. The oxidation number of the central element is lower by 2 in the “-ous” acid than in the “-ic” acid.

Thus, oxoacids of chlorine can be named as

| Formula           | Oxidation number | Name              |
|-------------------|------------------|-------------------|
| HClO              | +1               | hypochlorous acid |
| HClO <sub>2</sub> | +3               | chlorous acid     |
| HClO <sub>3</sub> | +5               | chloric acid      |
| HClO <sub>4</sub> | +7               | perchloric acid   |

**Problem-Solving Tip** Naming ternary acids and their anions.

| Decreasing oxidation number of central atom | Ternary acid    | Anion      | Decreasing number of oxygen atom of central atom |
|---------------------------------------------|-----------------|------------|--------------------------------------------------|
|                                             | PerXXXic acid   | PerXXXate  |                                                  |
|                                             | XXXic acid      | XXXate     |                                                  |
|                                             | XXXous acid     | XXXite     |                                                  |
|                                             | hypoXXXous acid | hypoXXXite |                                                  |

The stem (XXX) represents the stem of the name e.g., “nitr”, “sulphur” or “chlor”

**Do you know .....**

Oxidation state of the central atom is equal to its period group number, except for halogen

| IIIA                                                       | IVA                                                                                                                            | VA                                                                                                                                                                                | VIA                                                                                                                             | VIIA                                                                                              |
|------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|
| H <sub>3</sub> <sup>+3</sup> BO <sub>3</sub><br>boric acid | H <sub>2</sub> <sup>+4</sup> CO <sub>3</sub><br>carbonic acid<br>H <sub>4</sub> <sup>+4</sup> SiO <sub>4</sub><br>silicic acid | HNO <sub>3</sub> <sup>+5</sup><br>nitric acid<br>H <sub>3</sub> <sup>+5</sup> PO <sub>4</sub><br>phosphoric acid<br>H <sub>3</sub> <sup>+5</sup> AsO <sub>4</sub><br>arsenic acid | H <sub>2</sub> <sup>+6</sup> SO <sub>4</sub><br>sulphuric acid<br>H <sub>2</sub> <sup>+6</sup> SeO <sub>4</sub><br>selenic acid | H <sup>+5</sup> ClO <sub>3</sub><br>chloric acid<br>H <sup>+5</sup> IO <sub>3</sub><br>iodic acid |

**Illustration 1** What is the name of ClO<sup>-</sup> ion?

**Solution** We have

Oxidation number of Cl =  $x$

Oxidation number of O = -2

Total charge on ion = -1

Thus, O.N.(Cl) + O.N.(O) = total charge

$x - 2 = -1 \therefore x = +1$

Since, it is an oxoanion, hence it ends with ate. Thus it is chlorate (I) ion.

**Note :** Its common name is hypochlorite.

**Illustration 2** What is the formula of

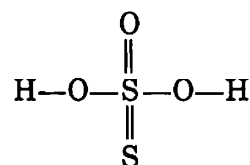
(a) iron (II) chloride (b) iron (III) chloride

(c) copper (II) nitrate

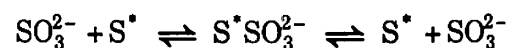
**Solution** (a) FeCl<sub>2</sub> (b) FeCl<sub>3</sub> (c) Cu(NO<sub>3</sub>)<sub>2</sub>

**Illustration 3** Thiosulphuric acid (a dibasic acid contains one sulphur and three oxygen atoms directly joined to central sulphur atom. What is oxidation number of sulphur atom?

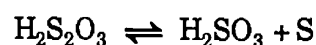
**Solution** Thiosulphuric acid is a dibasic acid represented as



The difference in the environment of two S-atoms shown by radioactive tracer studies using <sup>35</sup>S (a radioactive isotope of sulphur)



Thiosulphuric acid H<sub>2</sub>S<sub>2</sub>O<sub>3</sub> decomposes into sulphurous acid (H<sub>2</sub>SO<sub>3</sub>) and sulphur and the entire radioactivity is found associated with sulphur atom.



Thus, oxidation number of terminal S atom H<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = -2

and oxidation number of central S-atom in H<sub>2</sub>S<sub>2</sub>O<sub>3</sub> =  
net oxidation number of two S-atom = 4  
oxidation number per sulphur atom = +2

Table 4.4 Some Non-zero Oxidation States\* (Numbers)

|        |    |      |     |    |     |      |         |    |    |    |     |      |     |    |     |    |    |
|--------|----|------|-----|----|-----|------|---------|----|----|----|-----|------|-----|----|-----|----|----|
| IA     |    |      |     |    |     |      |         |    |    |    |     | VIIA |     | 0  |     |    |    |
| 1      |    |      |     |    |     |      |         |    |    |    |     | 1    | 2   |    |     |    |    |
| H      |    |      |     |    |     |      |         |    |    |    |     | H    | He  |    |     |    |    |
| +1     |    |      |     |    |     |      |         |    |    |    |     | +1   |     |    |     |    |    |
| -1     |    |      |     |    |     |      |         |    |    |    |     | -1   |     |    |     |    |    |
| IIA    |    |      |     |    |     |      |         |    |    |    |     | IIIA | IVA | VA | VIA |    |    |
| 3      | 4  |      |     |    |     |      |         |    |    |    |     | 5    | 6   | 7  | 8   | 9  | 10 |
| Li     | Be |      |     |    |     |      |         |    |    |    |     | B    | C   | N  | O   | F  | Ne |
| +1     | +2 |      |     |    |     |      |         |    |    |    |     | +3   | +4  | +5 | -1  | -1 |    |
|        |    |      |     |    |     |      |         |    |    |    |     |      | +2  | +4 | -2  |    |    |
|        |    |      |     |    |     |      |         |    |    |    |     |      | -4  | +3 |     |    |    |
|        |    |      |     |    |     |      |         |    |    |    |     |      |     | +2 |     |    |    |
|        |    |      |     |    |     |      |         |    |    |    |     |      |     | +1 |     |    |    |
|        |    |      |     |    |     |      |         |    |    |    |     |      |     | -3 |     |    |    |
| 11     | 12 |      |     |    |     |      |         |    |    |    |     | 13   | 14  | 15 | 16  | 17 | 18 |
| Na     | Mg |      |     |    |     |      |         |    |    |    |     | Al   | Si  | P  | S   | Cl | Ar |
| +1     | +2 |      |     |    |     |      |         |    |    |    |     | +3   | +4  | +5 | +6  | +7 |    |
|        |    |      |     |    |     |      |         |    |    |    |     |      | -4  | +3 | +4  | +5 |    |
|        |    |      |     |    |     |      |         |    |    |    |     |      |     | -3 | -2  | +3 |    |
|        |    |      |     |    |     |      |         |    |    |    |     |      |     |    |     | +1 |    |
|        |    |      |     |    |     |      |         |    |    |    |     |      |     |    |     | -1 |    |
| Groups |    |      |     |    |     |      |         |    |    |    |     |      |     |    |     |    |    |
|        |    | IIIB | IVB | VB | VIB | VIIB | (VIIIB) |    |    | IB | IIB |      |     |    |     |    |    |
| 19     | 20 | 21   | 22  | 23 | 24  | 25   | 26      | 27 | 28 | 29 | 30  | 31   | 32  | 33 | 34  | 35 | 36 |
| K      | Ca | Sc   | Ti  | V  | Cr  | Mn   | Fe      | Co | Ni | Cu | Zn  | Ga   | Ge  | As | Se  | Br | Kr |
| +1     | +2 | +3   | +4  | +5 | +6  | +7   | +3      | +3 | +2 | +2 | +2  | +3   | +4  | +5 | +6  | +7 | +4 |
|        |    |      | +3  | +4 | +3  | +6   | +2      | +2 |    | +1 |     |      | -4  | +3 | +4  | +5 | +2 |
|        |    |      | +2  | +3 | +2  | +4   |         |    |    |    |     |      |     | -3 | -2  | +3 |    |
|        |    |      |     | +2 |     | +3   |         |    |    |    |     |      |     |    |     | +1 |    |
|        |    |      |     |    |     | +2   |         |    |    |    |     |      |     |    |     | -1 |    |

O.N. shown in bold are common

**Illustration 4** Determine change in oxidation number in of the underlined of the following conversions:(a)  $\underline{\text{Cl}}^-$  changes to  $\text{ClO}_4^-$  (b)  $\underline{\text{Mn}}\text{O}_4^-$  changes to  $\text{MnO}_2$ (c)  $\underline{\text{C}}_2\text{O}_4^{2-}$  changes to  $\text{CO}_2$  (d)  $\underline{\text{Cr}}_2\text{O}_7^{2-}$  to  $\text{Cr}^{3+}$ **Solution**

| Oxidation number of the underlined                |                       |              |
|---------------------------------------------------|-----------------------|--------------|
| In reactant                                       | In product            | change       |
| (a) $\underline{\text{Cl}}^- = -1$                | $\text{ClO}_4^- = +7$ | 8            |
| (b) $\underline{\text{Mn}}\text{O}_4^- = +7$      | $\text{MnO}_2 = +4$   | 3            |
| (c) $\underline{\text{C}}_2\text{O}_4^{2-} = +3$  | $\text{CO}_2 = +4$    | 1 (per atom) |
| (d) $\underline{\text{Cr}}_2\text{O}_7^{2-} = +6$ | $\text{Cr}^{3+} = +3$ | 3 (per atom) |

**Illustration 5**  $\text{H}_2\text{O}_2$  changes to  $\text{O}_2$  or  $\text{H}_2\text{O}$  depending on the medium. What is change in oxidation number of oxygen per atom?**Solution** (i)  $\text{H}_2\text{O}_2 \longrightarrow \text{O}_2$ 

$$\begin{array}{ccc} \uparrow & & \\ -2 & & 0 \end{array}$$
 for every two oxygen atoms

Total change in oxidation number = 2 units

Change in oxidation number per atom = 1 unit

(ii)  $\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O}$ 

$$\begin{array}{ccc} & \nwarrow & \\ -2 & & -4 \end{array}$$
 coefficient 2 is used to balance O  
 oxidation number of two O-atoms

Total change in oxidation number = 2 units

Change in oxidation number per atom = 1 unit

**Illustration 6**  $\text{SO}_2$  under atmospheric condition changes to  $\text{SO}_4^{2-}$ . If oxidation number of S in  $\text{SO}_4^{2-}$  is +6, what is  $\text{SO}_2$ ?**Solution** Oxidation number of S in  $\text{SO}_4^{2-} = +6$ 

Oxidation number of O = -2

Thus,

$$\begin{array}{c} \text{S} \quad \text{O}^{2-} \\ \uparrow \quad \uparrow \\ 6 - 2x = -2 \\ 2x = 8 \end{array}$$

 $\therefore$ 

$$x = 4$$

Thus,

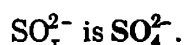


**Illustration 7** Match the species with correct oxidation number of the underlined:

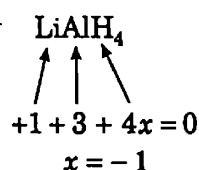
| Species                                     |      | Oxidation number |
|---------------------------------------------|------|------------------|
| A: <u>Cr</u> O <sub>2</sub> Cl <sub>2</sub> | I:   | +7               |
| B: <u>Mn</u> O <sub>3</sub> Cl              | II:  | +1               |
| C: <u>N</u> H <sub>2</sub> OH               | III: | +6               |
| D: <u>O</u> F <sub>2</sub>                  | IV:  | +2               |
| E: <u>N</u> <sub>2</sub> O                  | V:   | -1               |

**Solution**

| Species | O.N. |
|---------|------|
| A       | +6   |
| B       | +7   |
| C       | -1   |
| D       | +2   |
| E       | +1   |

**Illustration 8** What is the oxidation state of hydrogen in LiAlH<sub>4</sub>? Write an equation for the reaction of hydrogen in that oxidation state with water.

**Solution**



Thus, hydrogen is in the form of hydride (H<sup>-</sup>) in LiAlH<sub>4</sub>.

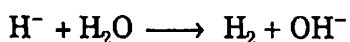
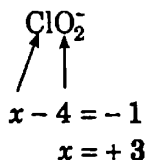


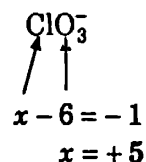
**Illustration 9** What is the oxidation number of Cl in

(a) Ca(ClO<sub>2</sub>)<sub>2</sub> (b) Ba(ClO<sub>3</sub>)<sub>2</sub> (c) CaOCl<sub>2</sub>?

**Solution** (a) Ca(ClO<sub>2</sub>)<sub>2</sub> has chlorite ion ClO<sub>2</sub><sup>-</sup>



(b) Ba(ClO<sub>3</sub>)<sub>2</sub> has chlorate ion ClO<sub>3</sub><sup>-</sup>



(c) CaOCl<sub>2</sub> is bleaching powder having two types of chlorine, Cl<sup>-</sup> and ClO<sup>-</sup> (hypochlorite ion)

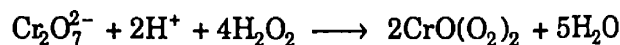
oxidation number of Cl in Cl<sup>-</sup> = -1

and oxidation number of Cl in ClO<sup>-</sup> = +1

Thus, in combined state oxidation number = 0

**Illustration 10** In qualitative analysis, a confirmatory test for chromate ion involves the formation of blue transient peroxo species, CrO<sub>5</sub>, which is better represented as CrO(O<sub>2</sub>)<sub>2</sub>. It is formed when H<sub>2</sub>O<sub>2</sub> is added to an acidic solution containing Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>. What is oxidation state of Cr in CrO(O<sub>2</sub>)<sub>2</sub>? Write the equation of formation of CrO<sub>5</sub>.

**Solution**



Oxidation state of oxygen in peroxide = -1

Oxidation state of oxygen in oxide = -2

Hence in,

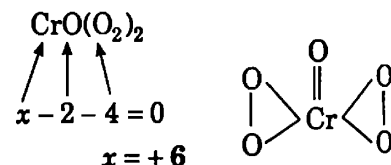
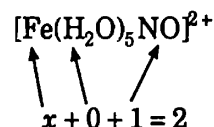


**Illustration 11** The complex [Fe(H<sub>2</sub>O)<sub>5</sub>NO]<sup>2+</sup> is formed in the 'ring-test' for nitrate ion when freshly prepared FeSO<sub>4</sub> solution is added to aqueous solution of NO<sub>3</sub><sup>-</sup> followed by addition of conc. H<sub>2</sub>SO<sub>4</sub>. If NO exists as nitrosyl NO<sup>+</sup>, what is oxidation number of iron? Explain. Also calculate magnetic moment of Fe.

**Solution** Let oxidation state of Fe = x

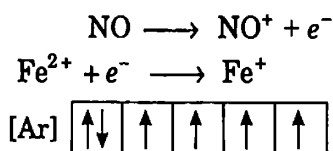


$\therefore$

$$x = +1$$

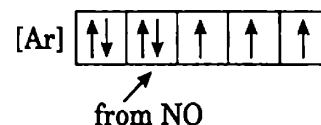
Thus, oxidation state of iron = +1

Iron is added as FeSO<sub>4</sub> with oxidation state of iron = +2. It is due to charge transfer from NO to Fe<sup>2+</sup>. NO changes to NO<sup>+</sup> and Fe<sup>2+</sup> to Fe<sup>+</sup>.



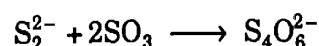
Electronic configuration of Fe<sup>2+</sup> = [Ar] 3d<sup>6</sup>

Fe<sup>2+</sup> gains one electron from NO hence, it has now three unpaired electrons (N = 3)



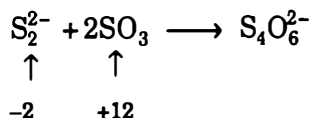
$$\begin{aligned} \text{Magnetic moment} &= \sqrt{N(N+2)} \text{ BM} = \sqrt{3 \times 5} \text{ BM} \\ &= \sqrt{15} = 3.873 \text{ BM} \end{aligned}$$

**Illustration 12** The tetrathionate anion, S<sub>4</sub>O<sub>6</sub><sup>2-</sup>, is a sulphur oxoanion derived from the compound tetrathionic acid, H<sub>4</sub>S<sub>4</sub>O<sub>6</sub>. Anion can be viewed as the adduct formed from the reaction between Lewis base S<sub>2</sub><sup>2-</sup> and Lewis acid SO<sub>3</sub>.



Two of the sulphur atoms are present in the oxidation state 0 and two are in oxidation state +5.

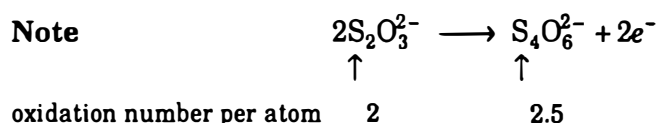
Alternately it can be explained as



Oxidation number of two sulphur atom in

Thus, oxidation number per sulphur atom =  $\frac{10}{4} = 2.5$

Note



## Target Practice 1

1. Oxidation number of Cr in  $\text{CrO}_2\text{Cl}_2$  is +6. What is oxidation number (per atom) of oxygen? .....

2.  $\text{H}_2\text{SO}_5 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ .

Derive oxidation number of sulphur in  $\text{H}_2\text{SO}_5$ .....

3. Write the common and IUPAC names of the following compounds.

|                     | Common | IUPAC |
|---------------------|--------|-------|
| (a) $\text{HIO}_3$  | .....  | ..... |
| (b) $\text{HClO}$   | .....  | ..... |
| (c) $\text{FeCl}_2$ | .....  | ..... |

(d)  $\text{Hg}_2\text{Cl}_2$  .....

(e)  $\text{Fe}(\text{NO}_3)_3$  .....

4. Chloride of a copper metal is colourless. What is its IUPAC name?

5. Compare basic strength of the following -

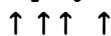
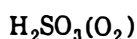
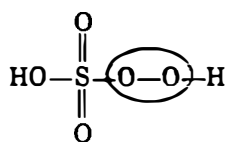
|                               |                      |                           |
|-------------------------------|----------------------|---------------------------|
| (a) $\text{H}_2\text{PO}_4^-$ | <input type="text"/> | $\text{H}_2\text{PO}_3^-$ |
| (b) $\text{HPO}_4^{2-}$       | <input type="text"/> | $\text{HPO}_3^{2-}$       |
| (c) $\text{ClO}^-$            | <input type="text"/> | $\text{ClO}_2^-$          |
| (d) $\text{NH}_3$             | <input type="text"/> | $\text{NH}_2^-$           |

## Answers

1.  $\text{CrO}_2\text{Cl}_2$   
 $\uparrow \quad \searrow \quad \swarrow$   
 $6 + 2x - 2 = 0$

Thus, x (oxidation number of oxygen) = -2

2. Formation of  $\text{H}_2\text{O}_2$  indicates that there is one peroxy linkage in  $\text{H}_2\text{SO}_5$ .

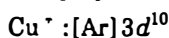
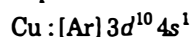


$$+2 + x - 6 - 2 = 0$$

x = 6. Thus, oxidation number of sulphur = +6

| 3.  | Common             | IUPAC                 |
|-----|--------------------|-----------------------|
| (a) | Iodic acid         | hydroiodic (V) acid   |
| (b) | hypochlorous acid  | hydrochloric (I) acid |
| (c) | ferrous chloride   | iron (II) chloride    |
| (d) | mercurous chloride | mercury (I) chloride  |
| (e) | ferric nitrate     | iron (III) nitrate    |

4. Since copper salt is colourless, it means there is no electron unpaired in d-orbital.



Thus, copper is +1

Thus, it is  $\text{Cu}_2\text{Cl}_2$  or  $\text{CuCl}$  : Copper (I) chloride

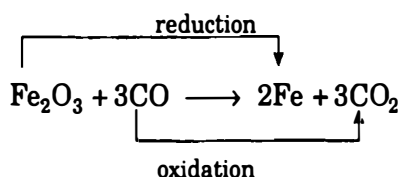
5. (a)  $\text{H}_2\text{PO}_4^- < \text{H}_2\text{PO}_3^-$  (b)  $\text{HPO}_4^{2-} < \text{HPO}_3^{2-}$   
 (c)  $\text{ClO}^- > \text{ClO}_2^-$  (d)  $\text{NH}_3 < \text{NH}_2^-$

## Oxidation and Reduction

### Oxidation and Reduction in Terms of Oxygen Transfer

- Oxidation is gain of oxygen.
- Reduction is loss of oxygen.

For example, in the extraction of iron from its ore :



Because both reduction and oxidation are going on side-by-side, this is known as a **redox** reaction.

### Oxidising and Reducing Agents

An oxidising agent is substance which oxidises something else. In the above example, the iron (III) oxide is the oxidising agent.

A reducing agent reduces something else. In the equation, the carbon monoxide is the reducing agent.

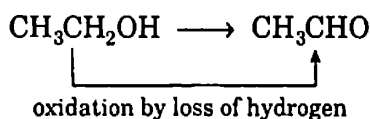
- Oxidising agents give oxygen to another substance.
- Reducing agents remove oxygen from another substance.

## Oxidation and Reduction in Terms of Hydrogen Transfer

- Oxidation is loss of hydrogen.
- Reduction is gain of hydrogen.

Notice that these are exactly the opposite of the oxygen definitions.

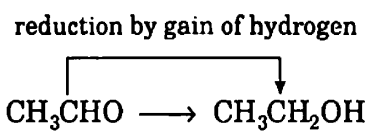
For example, ethanol can be oxidised to ethanal :



You would need to use an oxidising agent to remove the hydrogen from the ethanol. A commonly used oxidising agent is potassium dichromate (VI) solution acidified with dilute sulphuric acid.

**Note** The equation for this is rather complicated for this introductory page. If you are interested, you will find a similar example (ethanol to ethanoic acid) on the page dealing with writing equations for redox reactions.

Ethanal can also be reduced back to ethanol again by adding hydrogen to it. A possible reducing agent is sodium tetrahydridoborate,  $\text{NaBH}_4$ . Again the equation is too complicated to be worth bothering about at this point.



### DEEP Focus

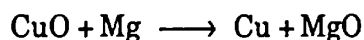
- Oxidising agents give oxygen to another substance or remove hydrogen from it.
- Reducing agents remove oxygen from another substance or give hydrogen to it.

## Oxidation and Reduction in Terms of Electron Transfer

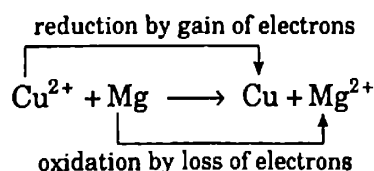
- Oxidation is loss of electrons.
- Reduction is gain of electrons.

|                   |  |                   |
|-------------------|--|-------------------|
| Oil               |  | Ring              |
| oxidation is loss |  | reduction is gain |

**A simple example** The equation shows a simple redox reaction which can obviously be described in terms of oxygen transfer.



Copper (II) oxide and magnesium oxide are both ionic. The metals obviously aren't. If you rewrite this as an ionic equation, it turns out that the oxide ions are spectator ions and you are left with:



If you look at the equation above, the magnesium is reducing the copper(II) ions by giving them electrons to neutralise the charge. Magnesium is a reducing agent.

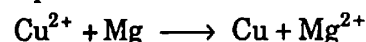
Looking at it the other way round, the copper (II) ions are removing electrons from the magnesium to create the magnesium ions. The copper (II) ions are acting as an oxidising agent.

## Writing Ionic Equations for Redox Reactions

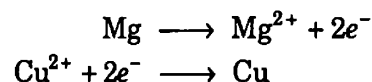
### Electron-Half-Equations

**What is an electron-half-equation?**

When magnesium reduces hot copper (II) oxide to copper, the ionic equation for the reaction is :



You can split the ionic equation into two parts, and look at it from the point of view of the magnesium and of the copper (II) ions separately. This shows clearly that the magnesium has lost two electrons, and the copper (II) ions have gained them.



These two equations are described as "electron-half-equations" or "half-equations" or "ionic-half-equations" or "half-reactions"

Any redox reaction is made up of two half-reactions : in one of them electrons are being lost (an oxidation process) and in the other one those electrons are being gained (a reduction process).

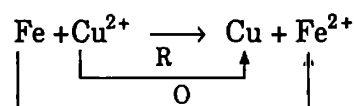
### DEEP Focus

- An oxidising agent oxidises something else.
- Oxidation is loss of electrons (OIL RIG), that means that an oxidising agent takes electrons from that other substance.
- So an oxidising agent must gain electrons.

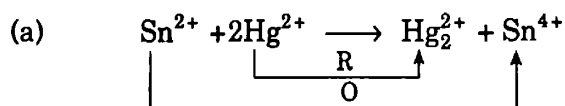
Or you could think it out like this :

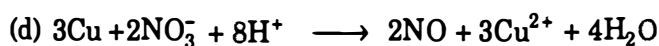
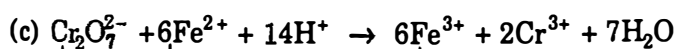
- An oxidising agent oxidises something else, that means that the oxidising agent must be being reduced.
- Reduction is gain of electrons (OIL RIG). so an oxidising agent must gain electrons.

A complete reaction showing oxidation and reduction together is called a **redox-reaction**.



Some examples of redox reactions are:



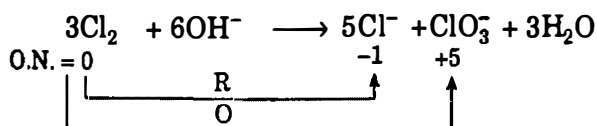


### DEEP Focus

If one of the half-reactions does not take place, other half will also not take place. We can say oxidation and reduction go side by side.

In the above examples, two substances react — one of them is an oxidising agent and the other is a reducing agent. Such reactions relate to intermolecular oxidation-reduction ones.

Consider the following example:



In this case we find that  $\text{Cl}_2$  has been oxidised as well as reduced. Such type of redox reaction is called **disproportionation** (autooxidation-autoreduction) reaction. Examples are:

- $$2\text{Cu}^+ \xrightarrow{\text{Disproportionates}} \text{Cu} + \text{Cu}^{2+}$$

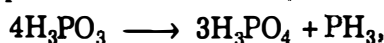
$\xrightarrow{\text{R}}$        $\xrightarrow{\text{O}}$
- $$2\text{HCHO} + \text{OH}^- \longrightarrow \text{CH}_3\text{OH} + \text{HCOO}^-$$

$\xrightarrow{\text{R}}$        $\xrightarrow{\text{O}}$
- $$4\text{ClO}_3^- \longrightarrow 3\text{ClO}_4^- + \text{Cl}^-$$

$\xrightarrow{\text{O}}$        $\xrightarrow{\text{R}}$
- $$3\text{MnO}_4^{2-} + 2\text{H}_2\text{O} \longrightarrow \text{MnO}_2 + 2\text{MnO}_4^- + 4\text{OH}^-$$

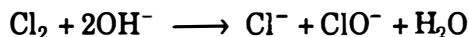
$\xrightarrow{\text{R}}$        $\xrightarrow{\text{O}}$
- $$\begin{array}{c} \text{CHO} \\ | \\ \text{CHO} \end{array} + \text{OH}^- \longrightarrow \begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{COO}^- \end{array}$$
- $$2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$$

In disproportionation reactions, compounds are simultaneously formed that contain a given element in a more oxidised and more reduced state than the initial one. The initial substance displays functions of both an oxidising and a reducing agent. Such reactions are possible if the relevant element is an intermediate oxidation in the initial compound. In the following disproportionation reaction,

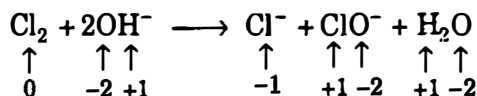


Oxidation number of P (in  $\text{H}_3\text{PO}_3$ ) is +3 which is the intermediate of +5 (in  $\text{H}_3\text{PO}_4$ ) and -3 (in  $\text{PH}_3$ ). Such substances have **oxidation-reduction duality**.

The reaction between chlorine and cold dilute sodium hydroxide solution is :



Obviously the chlorine has changed oxidation state because it has ended up in compounds starting from the original element. Checking all the oxidation states shows :



The chlorine is the only thing to have changed oxidation state. One atom has been reduced because its oxidation state has fallen. The other has been oxidised.

This is a good example of disproportionation reaction. A disproportionation reaction is one in which a single substance is both oxidised and reduced.

**Illustration 1** Write unbalanced oxidation and reduction half-reactions for the following processes:

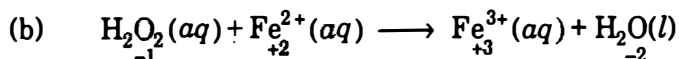
- $\text{Te(s)} + \text{NO}_3^-(\text{aq}) \longrightarrow \text{TeO}_2(\text{s}) + \text{NO(g)}$
- $\text{H}_2\text{O}_2(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \longrightarrow \text{Fe}^{3+}(\text{aq}) + \text{H}_2\text{O(l)}$
- $\text{Mn(s)} + \text{NO}_3^-(\text{aq}) \longrightarrow \text{Mn}^{2+}(\text{aq}) + \text{NO}_2(\text{g})$
- $\text{Mn}^{3+}(\text{aq}) \longrightarrow \text{MnO}_2(\text{s}) + \text{Mn}^{2+}(\text{aq})$

**Solution** (a)  $\text{Te(s)} + \text{NO}_3^-(\text{aq}) \longrightarrow \text{TeO}_2(\text{s}) + \text{NO(g)}$

$\begin{array}{ccc} 0 & +5 & +4 \end{array}$

**Oxidation :**  $\text{Te(s)} \longrightarrow \text{TeO}_2(\text{s})$

**Reduction :**  $\text{NO}_3^-(\text{aq}) \longrightarrow \text{NO(g)}$

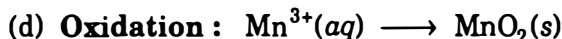


**Oxidation :**  $\text{Fe}^{2+}(\text{aq}) \longrightarrow \text{Fe}^{3+}(\text{aq})$

**Reduction :**  $\text{H}_2\text{O}_2(\text{aq}) \longrightarrow \text{H}_2\text{O(l)}$



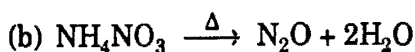
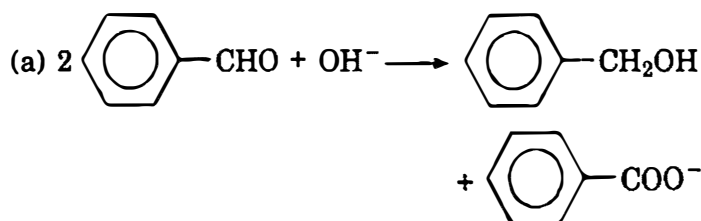
**Reduction :**  $\text{NO}_3^-(\text{aq}) \longrightarrow \text{NO}_2(\text{g})$

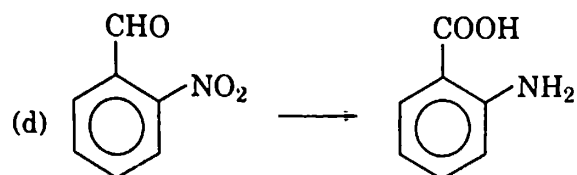
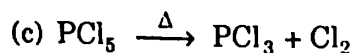


**Reduction :**  $\text{Mn}^{3+}(\text{aq}) \longrightarrow \text{Mn}^{2+}(\text{aq})$

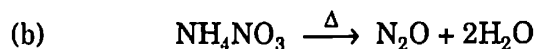
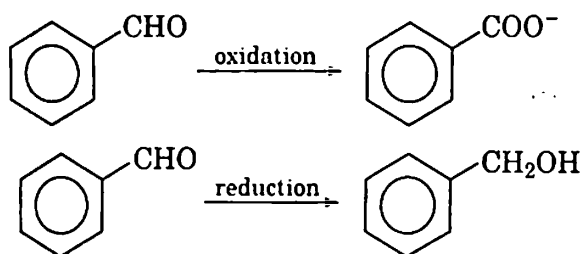
In this reaction,  $\text{Mn}^{3+}$  has been oxidised to  $\text{MnO}_2(\text{s})$  as well as reduced to  $\text{Mn}^{2+}(\text{aq})$ . Thus, it is a **disproportionation** reaction.

**Illustration 2** Identify the species oxidised and reduced in the following:





**Solution** (a) It is a case of Cannizzaro reaction.  $\text{RCHO}$  has been oxidised to  $\text{RCOO}^-$  as well as reduced to  $\text{RCH}_2\text{OH}$  in a proton-hydride transfer reaction. Thus, it is a disproportionation reaction.

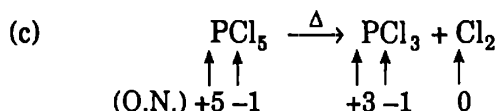


There are two types of nitrogen, one in  $\text{NH}_4^+$  ion (oxidation number = -3) and the other in  $\text{NO}_3^-$  (oxidation number = +5). On decomposition,  $\text{N}_2\text{O}$  (oxidation number = +1) is formed. Thus,  $\text{NH}_4^+$  is oxidised to  $\text{N}_2\text{O}$  and  $\text{NO}_3^-$  is reduced to  $\text{N}_2\text{O}$ .

But it is not the disproportionation reaction.

Both the elements are in the same initial substance.

Reactions of this kind are known as **intramolecular oxidation reduction reactions**.



Phosphorus (V) of  $\text{PCl}_5$  is thus reduced to P(III) of  $\text{PCl}_3$ . Cl (-1) is oxidised to  $\text{Cl}_2(0)$ .

(d)  $-\text{CHO}$  group is oxidised to  $-\text{COOH}$  and  $-\text{NO}_2$  group is reduced to  $-\text{NH}_2$ .

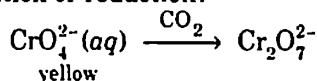
Thus, it is **intramolecular redox-reaction**.

## Target Practice 2

1.  $\text{I}^-$  changes to  $\text{I}_3^-$  in a reaction. Is it oxidation or reduction?



2. On passing  $\text{CO}_2$  into aqueous yellow coloured  $\text{CrO}_4^{2-}$  solution, an orange coloured  $\text{Cr}_2\text{O}_7^{2-}$  solution is obtained. This is oxidation or reduction?



3. Anhydride of an acid is formed by dehydration and oxidation number of central atom remains unchanged.

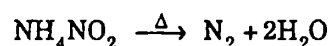
Acid:  $\text{H}_2\text{N}_2\text{O}_2, \text{HNO}_2, \text{HNO}_3$

Anhydride:  $\text{N}_2\text{O}_5, \text{N}_2\text{O}, \text{NO}, \text{N}_2\text{O}_3$

Match acid with anhydride.

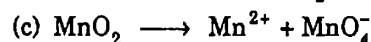
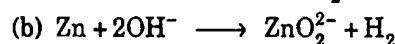
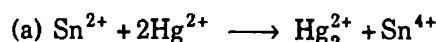
| Acid                             | Anhydride |
|----------------------------------|-----------|
| $\text{H}_2\text{N}_2\text{O}_2$ | .....     |
| $\text{HNO}_2$                   | .....     |
| $\text{HNO}_3$                   | .....     |

4.  $\text{NH}_4\text{NO}_2$  changes to  $\text{N}_2$  on heating.



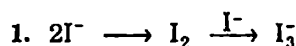
Indicate the species (i) oxidised (ii) reduced

5. Select oxidant and reductant in the following :

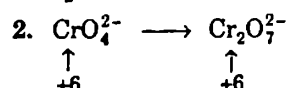


| Oxidant | Reductant |
|---------|-----------|
| .....   | .....     |
| .....   | .....     |
| .....   | .....     |

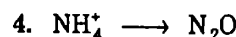
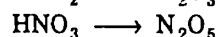
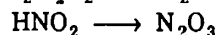
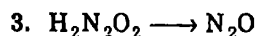
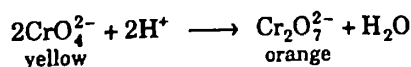
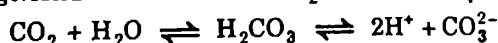
## Answers



$\text{I}^-$  is oxidised to  $\text{I}_2$  which is soluble in KI forming  $\text{KI}_3$  ( $\text{I}_3^-$ ). Thus,  $\text{I}_2$  is formed by oxidation.



In both anion, oxidation number of chromium is +6. Hence, no change. Acidic medium due to  $\text{CO}_2$  converts  $\text{CrO}_4^{2-}$  into  $\text{Cr}_2\text{O}_7^{2-}$ .



**Oxidation**



**Reduction**

- 5.

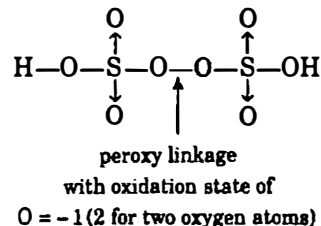
|     | Oxidant          | Reductant        |
|-----|------------------|------------------|
| (a) | $\text{Hg}^{2+}$ | $\text{Sn}^{2+}$ |
| (b) | $\text{OH}^-$    | $\text{Zn}$      |
| (c) | $\text{MnO}_2$   | $\text{MnO}_2$   |

## Practice Exercise 1

- What is oxidation number of carbon in  $\text{CN}^-$ ?
- What is the change in oxidation number of the underlined atom in following conversions?
  - $\text{NaH}\underline{\text{C}}\text{O}_3 + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$
  - $2\text{NaOH} + \underline{\text{B}}\text{r}_2 \longrightarrow \text{NaBr} + \text{NaBrO} + \text{H}_2\text{O}$
  - $\text{K}\underline{\text{I}} \longrightarrow \text{KIO}_3$
  - $\text{H}_2\underline{\text{S}}\text{O}_6 + 2\text{K}\underline{\text{I}} \longrightarrow \text{K}_2\text{SO}_4 + \text{H}_2\text{O} + \text{I}_2$
  - $2\text{H}\underline{\text{N}}\text{O}_3 \longrightarrow \text{H}_2\text{O} + \text{N}_2\text{O}_5$
  - $\text{CaO}\underline{\text{C}}\text{l}_2 + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + \text{Cl}_2$
  - $\underline{\text{Mn}}\text{O}_4^- + 3\text{OH}^- \longrightarrow \text{MnO}_2 + \text{H}_2\text{O}$  (dil.)
  - $\underline{\text{As}}_2\text{S}_3 + \text{OH}^- \longrightarrow \text{AsS}_3^{3-}$
- In  $\text{H}_2\text{S}_2\text{O}_8$  oxidation state of sulphur is six? Explain by structure.
- Write a formula for
  - sulphate of iron with Fe in the oxidation state +3.
  - an oxoacid of nitrogen with N in the oxidation state +3.
  - an oxide of chlorine with Cl in the oxidation state +7.
- Which is the anhydride of  $\text{HNO}_3$  out of  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}_5$ ?
- Which is stronger base in each pair?
  - $\text{HSO}_4^-$ ,  $\text{HSO}_3^-$
  - $\text{NO}_2^-$ ,  $\text{NO}_3^-$
  - $\text{Cl}^-$ ,  $\text{ClO}^-$
- $\text{VO}_2^{2+}$  and  $\text{VO}^{2+}$  are known as vanadyl ion. Determine oxidation number of vanadium in each.
- Assign oxidation numbers to each atom in the following substances:
  - ethane ( $\text{C}_2\text{H}_6$ )
  - borax ( $\text{Na}_2\text{B}_4\text{O}_7$ )
  - silicate mineral of magnesium ( $\text{Mg}_2\text{Si}_2\text{O}_6$ )
- What is the type of linkage in  $(\text{NH}_3)_3\text{CrO}_4$  if oxidation number of Cr is +4?
  - $\text{K}_3\text{Cr}(\text{O}_2)_x$  has peroxy linkage with oxidation number of Cr as +5. What is value of  $x$ ?
- Determine the oxidation state of the underlined element in:
  - $\text{K}_4\underline{\text{P}}_2\text{O}_7$
  - $\text{K}\underline{\text{Au}}\text{Cl}_4$
  - $\text{Rb}_4\text{Na}[\underline{\text{H}}\underline{\text{V}}_{10}\text{O}_{28}]$
  - $\underline{\text{I}}\text{Cl}$
  - $\text{Ba}(\underline{\text{C}}\text{O})_2$
  - $\underline{\text{O}}\text{F}_2$
  - $\text{Ba}_2\underline{\text{Xe}}\text{O}_6$
- Identify oxidant and reductant in the following redox reactions:
  - $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \longrightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$
  - $2\text{K}_2\text{MnO}_4 + \text{Cl}_2 \longrightarrow 2\text{KCl} + 2\text{KMnO}_4$
  - $2\text{MnO}_4^{2-} + 2\text{H}_2\text{O} \xrightarrow{\text{current}} 2\text{MnO}_4^- + 2\text{OH}^- + \text{H}_2$
  - $\text{P}_4 + 5\text{O}_2 \longrightarrow \text{P}_4\text{O}_{10}$
  - $\text{Hg}^{2+} + \text{NO}_2^- + \text{H}_2\text{O} \longrightarrow \text{Hg} + \text{NO}_3^- + 2\text{H}^+$
- Identify disproportionation reactions in the following:
  - $3\text{MnO}_4^{2-} + 4\text{H}^+ \longrightarrow \text{MnO}_2 + 2\text{MnO}_4^- + 2\text{H}_2\text{O}$
  - $2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$
  - $2\text{C}_6\text{H}_5\text{CHO} + \text{OH}^- \longrightarrow \text{C}_6\text{H}_5\text{COO}^- + \text{C}_6\text{H}_5\text{CH}_2\text{OH}$
  - $2\text{CH}_3\text{CHO} \xrightarrow{\text{Al(OEt)}_3} \text{CH}_3\text{COOCH}_2\text{CH}_3$
  - $4\text{H}_3\text{PO}_3 \xrightarrow{\Delta} 3\text{H}_3\text{PO}_4 + \text{PH}_3$
  - $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \xrightarrow{\Delta} 3\text{NaH}_2\text{PO}_2 + \text{PH}_3$
  - $\text{NH}_4\text{NO}_3 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$
- Underline the species which are oxidised and reduced in the following (unbalanced) reactions:
  - $\text{CN}^- + \text{OCl}^- \longrightarrow \text{N}_2 + \text{HCO}_3^- + \text{Cl}^-$
  - $\text{C}_6\text{H}_5\text{OH} + \text{O}_3 \longrightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{O}_2$
  - $\text{I}^- + \text{O}_3 \longrightarrow \text{O}_2 + \text{I}_2$
  - $\text{S}_2\text{O}_3^{2-} + \text{Cl}_2 \longrightarrow \text{HSO}_4^- + \text{Cl}^-$
  - $\text{C} + \text{ZnO} \longrightarrow \text{Zn} + \text{CO}$
- Classify each of the following unbalanced half-reactions as either an oxidation or a reduction:
  - $\text{O}_2(\text{g}) \longrightarrow \text{OH}^-(\text{aq})$
  - $\text{H}_2\text{O}_2(\text{aq}) \longrightarrow \text{O}_2(\text{g})$
  - $\text{MnO}_4^-(\text{aq}) \longrightarrow \text{MnO}_2^-(\text{aq})$
  - $\text{CH}_3\text{OH}(\text{aq}) \longrightarrow \text{CH}_2\text{O}(\text{aq})$

## Answers

- +2 (Hint: In the cyanide ion,  $\text{CN}^-$ , N is more electronegative than C and taking the common negative oxidation state of N as -3, oxidation state of C = +2)
- No change
  - Decreases to -1, w.r.t. NaBr and increases to +1 w.r.t. NaBrO
  - 6
  - No change in S of  $\text{H}_2\text{SO}_5$  (since its peroxy linkage is affected) and 1 in KI
  - No change
  - There are two types of Cl in  $\text{CaOCl}_2$ .  $\text{Cl}^-$  (oxidation number = -1) and Cl in  $\text{ClO}^-$  (oxidation number = +1)  $\text{Cl}^-$  is oxidised to  $\text{Cl}_2$  and  $\text{ClO}^-$  is reduced to  $\text{Cl}_2$  we find overall change is zero (since in  $\text{CaOCl}_2$  total oxidation number is 0)
  - 3 (h) 2
- $\text{H}_2\text{S}_2\text{O}_8$  (called Marshall's acid) is peroxy disulphuric acid as shown;



Other six oxygen atoms have oxidation state of -2 each, hence, **oxidation state of sulphur is six** :

$$2x + 2(\text{for two H}) - 12(\text{for six O}) - 2(\text{peroxy}) = 0$$

$$\therefore x = 6 \text{ per sulphur atom}$$

- $\text{Fe}_2(\text{SO}_4)_3$
  - $\text{HNO}_2$
  - $\text{Cl}_2\text{O}_7$
- $\text{N}_2\text{O}_5$  (oxidation number of the element (N) in oxyacid and its anhydride remains same).
- $\text{HSO}_3^-$
  - $\text{NO}_2^-$
  - $\text{Cl}^-$

Smaller the oxidation number, stronger the conjugate base.
- +6 in  $\text{VO}_2^{2+}$  and +4 in  $\text{VO}^{2+}$



8. (a) C = -3, H = +1 (b) Na = +1, B = +3, O = -2  
(c) Mg = +2, Si = +4, O = -2

9. (a)  $(\text{NH}_3)_3\text{CrO}_4$ , take oxidation number of O = x  

$$\begin{array}{ccc} \uparrow & \uparrow & \uparrow \\ 0 & +4 & +4x = 0 \end{array}$$

$$x = -1$$

Thus, oxygen atoms are in the form of peroxy linkage. The compound can be written as  $(\text{NH}_3)_3\text{Cr}(\text{O}_2)_2$ .

- (b)  $\text{K}_3\text{Cr}(\text{O}_2)_x$  has  $\text{Cr}(\text{O}_2)_x^{3-}$  ion

$$\begin{array}{c} \text{Cr}(\text{O}_2)_x^{3-} \\ \uparrow \uparrow \\ +5 - 2x = -3 \\ -2x = -8 \\ x = 4 \end{array}$$

It is  $\text{K}_3\text{Cr}(\text{O}_2)_4$

10. (a) P = +5 (b) Au = +3 (c) V = +5 (d) I = +1  
(e) Cl = +3 (f) O = +2 (g) Xe = +8

11. **Oxidant                      Reductant**

- |                          |                          |
|--------------------------|--------------------------|
| (a) $\text{O}_2$         | $\text{MnO}_2$           |
| (b) $\text{Cl}_2$        | $\text{K}_2\text{MnO}_4$ |
| (c) $\text{H}_2\text{O}$ | $\text{MnO}_4^{2-}$      |
| (d) $\text{O}_2$         | $\text{P}_4$             |
| (e) $\text{Hg}^{2+}$     | $\text{NO}_2^-$          |

12. (a)  $\text{MnO}_4^{2-}$  is reduced to  $\text{MnO}_2$  as well as oxidised to  $\text{MnO}_4^-$  hence, disproportionation.

- (b) Cl of  $\text{KClO}_3$  (O.N. = +5) is reduced to  $\text{Cl}^-$  and O of  $\text{KClO}_3$  (O.N. = -2) is oxidised to  $\text{O}_2$  hence, redox but not disproportionation.  
(c)  $\text{C}_6\text{H}_5\text{CHO}$  is oxidised to  $\text{C}_6\text{H}_5\text{COO}^-$  as well as reduced to  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  (Cannizzaro reaction) hence disproportionation.  
(d)  $\text{CH}_3\text{COOC}_2\text{H}_5$  (ester) is formed from  $\text{CH}_3\text{COOH}$  (oxidation product of  $\text{CH}_3\text{CHO}$ ) and  $\text{CH}_3\text{CH}_2\text{OH}$  (reduction product of  $\text{CH}_3\text{CHO}$ ), hence  $\text{CH}_3\text{CHO}$  disproportionates in presence of aluminium ethoxide (Tischenko reaction).  
(e)  $\text{H}_3\text{PO}_3$  (O.N. of P = +3) disproportionates to  $\text{H}_3\text{PO}_4$  (O.N. of P = +5) and  $\text{PH}_3$  (O.N. of P = -3).  
(f)  $\text{P}_4$  (O.N. = 0) disproportionates to  $\text{NaH}_2\text{PO}_2$  (O.N. of P = +1) and  $\text{PH}_3$  (O.N. of P = -3).  
(g)  $\text{NH}_4^+$  (O.N. of N = -3) oxidises to  $\text{N}_2\text{O}$  (O.N. of N = +1).  $\text{NO}_3^-$  (O.N. of N = +5) reduces to  $\text{N}_2\text{O}$ ; hence redox but not disproportionation.

13. (a) Oxidation of C (O.N. = +2) and N (O.N. = -3) of  $\text{CN}^-$  into  $\text{HCO}_3^-$  (O.N. of C = +4) and  $\text{N}_2$  (O.N. of N = 0) respectively and reduction of  $\text{OCl}^-$  (O.N. of Cl = +1) into  $\text{Cl}^-$  (O.N. of Cl = -1).  
(b) Oxidation of  $\text{C}_6\text{H}_5\text{OH}$  into  $\text{CO}_2$  by  $\text{O}_3$   
(c) Oxidation of  $\text{I}^-$  into  $\text{I}_2$  by  $\text{O}_3$   
(d) Oxidation of  $\text{S}_2\text{O}_3^{2-}$  into  $\text{HSO}_4^-$  by  $\text{Cl}_2$   
(e)  $\text{ZnO}$  is reduced to  $\text{Zn}$
14. (a) Reduction (b) Oxidation (c) Reduction  
(d) Oxidation

## Do you Know .....

A redox predominance diagram shows the predominant (thermodynamically most stable) oxidation state and chemical form of an element at any given potential. In this type of diagram, elements with no redox chemistry (such as Ar) will predominate at all potentials and will cover the entire diagram. Among those with more than one thermodynamically stable oxidation state, more strongly oxidising stable chemical forms are confined to higher regions of redox predominance diagrams. Correspondingly strongly reducing stable chemical forms will be low in the predominance diagrams Fig 4.1 represents redox predominance diagram of iron. Of the chemical forms of iron shown, the most strongly oxidising is the ferrate ion,  $\text{FeO}_4^{2-}$ ; the most strongly reducing is iron metal, Fe.

| Oxidation state | Half-reaction                                                                                           | $E^\circ/\text{V}$ |
|-----------------|---------------------------------------------------------------------------------------------------------|--------------------|
| +6              | $\text{FeO}_4^{2-} + 8\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{Fe}^{3+} + 4\text{H}_2\text{O}$ | +2.20 V            |
| +3              | $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$                                         | +0.77 V            |
| +2              | $\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe(s)}$                                          | -0.44 V            |
|                 |                                                                                                         | Fe                 |

Fig. 4.1 Redox predominance diagram for the element iron, with the corresponding reduction half-reactions

## How to Balance a Redox Reaction?

Working out electron-half-equations and using them to build ionic equations.

### Illustration 1 The reaction between chlorine and iron (II) ions

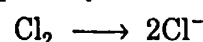
Chlorine gas oxidises iron (II) ions to iron (III) ions. In the process, the chlorine is reduced to chloride ions.

You would have to know this, or be told it by an examiner. In building equations, there is quite a lot that you can work out as you go along, but you have to have somewhere to start from!

You start by writing down what you know for each of the half-reactions. In the chlorine case, you know that chlorine (as molecules) turns into chloride ions :



The first thing to do is to balance the atoms that you have got as far as you possibly can :



Always check that you have the existing atoms balanced before you do anything else. If you forget to do this, everything else that you do after wards is a complete waste of time!

Now you have to add things to the half-equation in order to make it balance completely.

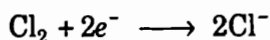
All you are allowed to add are :

- electrons
- water

- hydrogen ions (unless the reaction is being done under alkaline conditions in which case, you can add hydroxide ions instead)

In the chlorine case, all that is wrong with the existing equation that we've produced so far is that the charges don't balance. The left-hand side of the equation has no charge, but the right-hand side carries 2 negative charges.

That's easily put right by adding two electrons to the left-hand side. The final version of the half-reaction is :

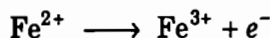


Now you repeat this for the iron (II) ions. You know (or are told) that they are oxidised to iron (III) ions. Write this down :

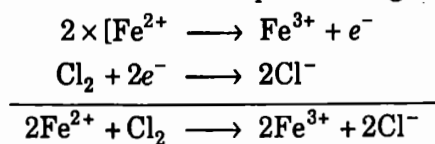


The atoms balance, but the charges don't. There are 3 positive charges on the right-hand side, but only 2 on the left.

You need to reduce the number of positive charges on the right-hand side. That's easily done by adding an electron to that side :



It is obvious that the iron reaction will have to happen twice for every chlorine molecule that reacts. Allow for that, and then add the two half-equations together.



But don't stop there!! Check that everything balances-atoms and charges. It is very easy to make small mistakes, especially if you are trying to multiply and add up more complicated equations.

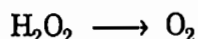
### Illustration 2 The reaction between hydrogen peroxide and manganate (VII) ions

The first example was a simple bit of chemistry which you may well have come across. The technique works just as well for more complicated (and perhaps unfamiliar) chemistry.

Manganate (VII) ions,  $\text{MnO}_4^-$ , oxidise hydrogen peroxide,  $\text{H}_2\text{O}_2$ , to oxygen gas. The reaction is done with potassium manganate (VII) solution and hydrogen peroxide solution acidified with dilute sulphuric acid.

During the reaction, the manganate (VII) ions are reduced to manganese (II) ions.

Let's start with the hydrogen peroxide half-equation. What we know is :

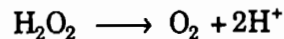


The oxygen is already balanced. What about the hydrogen?

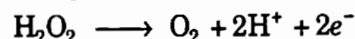
All you are allowed to add to this equation are water, hydrogen ions and electrons. If you add water to supply the extra hydrogen atoms needed on the right-hand side,

you will mess up the oxygens again-that's obviously wrong!

Add two hydrogen ions to the right-hand side.

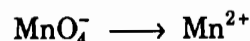


Now all you need to do is balance the charges. You would have to add 2 electrons to the right-hand side to make the overall charge on both sides zero.



Now for the manganate(VII) half-equation:

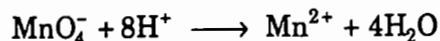
You know (or are told) that the manganate(VII) ions turn into manganese(II) ions. Write that down.



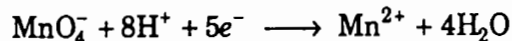
The manganese balances, but you need four oxygens on the right-hand side. These can only come from water-that's the only oxygen-containing thing you are allowed to write into one of these equations in acid conditions.



By doing this, we've introduced some hydrogens. To balance these, you will need 8 hydrogen ions on the left-hand side.



Now that all the atoms are balanced, all you need to do is balance the charges. At the moment there are a net 7+ charges on the left-hand side (1- and 8+), but only 2+ on the right. Add 5 electrons to the left-hand side to reduce the 7+ to 2+.



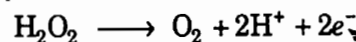
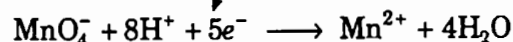
This is the typical sort of half-equation which you will have to be able to work out. The sequence is usually :

- Balance the atoms apart from oxygen and hydrogen.
- Balance the oxygens by adding water molecules.
- Balance the hydrogens by adding hydrogen ions.
- Balance the charges by adding electrons.

*Combining the half-reactions to make the ionic equation for the reaction*

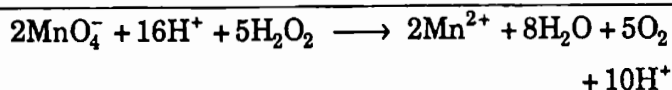
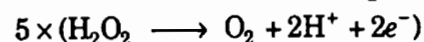
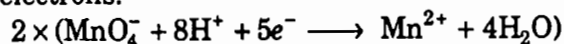
The two half-equations we've produced are :

This reaction needs 5 electrons

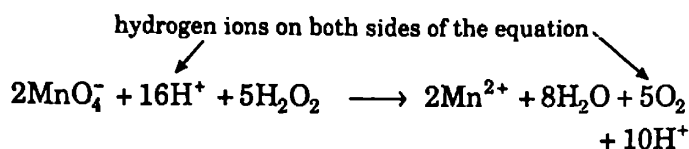


but this is only producing 2 electrons

You have to multiply the equations so that the same number of electrons are involved in both. In this case, everything would work out well if you transferred 10 electrons.



But this time, you haven't quite finished. During the checking of the balancing, you should notice that there are hydrogen ions on both sides of the equation :



You can simplify this down by subtracting 10 hydrogen ions from both sides to leave the final version of the ionic equation—but don't forget to check the balancing of the atoms and charges!



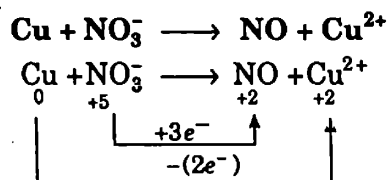
You will often find that hydrogen ions or water molecules appear on both sides of the ionic equation in complicated cases built up in this way. Always check, and then simplify where possible.

## Working out oxidation number and using them to balance equation

In the entrance examination it is never mentioned what method is to be used. We adopt here "quick" method that will certainly be a time-saving method.

### Acidic Medium

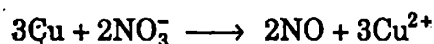
**Illustration 1** We want to balance following equation:



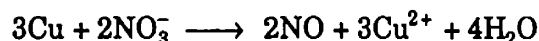
#### ALERT

- Affected atoms are balanced.
- Take total O.N. of the affected atom on each side.

(a) Cross multiply by change in O.N.



(b) Balance oxygen by  $\text{H}_2\text{O}$



(c) Balance hydrogen by  $\text{H}^+$

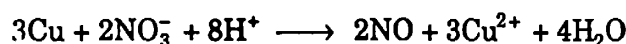
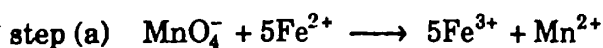
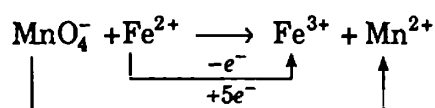


**Illustration 2**  $\text{MnO}_4^- + \text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{Mn}^{2+}$

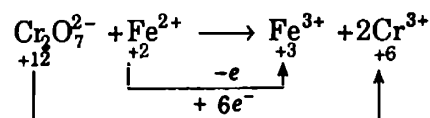


step (c)



**Illustration 3**  $\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{Cr}^{3+}$

In this Cr atoms on RHS are not balanced. Hence, first step is to balance  $\text{Cr}^{3+}$  and take O.N. of two Cr atoms



By taking steps of illustration (1), balanced equation is

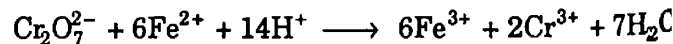
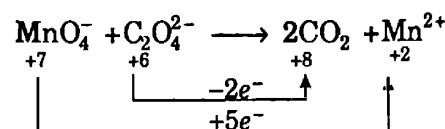


**Illustration 4**  $\text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{CO}_2 + \text{Mn}^{2+}$



Carbon atoms are taken balanced and taking usual steps:

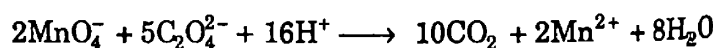
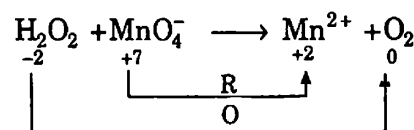
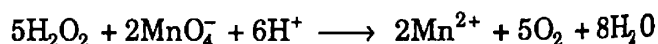


**Illustration 5**  $\text{H}_2\text{O}_2 + \text{MnO}_4^- \longrightarrow \text{Mn}^{2+} + \text{O}_2$

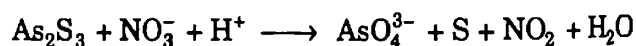


$\text{H}_2\text{O}_2$  has been oxidised to  $\text{O}_2$ . Thus, oxygen atoms undergoing oxidation are balanced. Taking O.N. of both oxygen and as by usual steps, balanced equation is

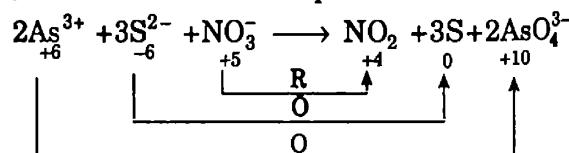


Total H on LHS = (double of  $\text{H}_2\text{O}$ ) – (H of  $\text{H}_2\text{O}_2$ )

**Illustration 6** We may face some difficulties when two or more atoms are oxidised or reduced. In the following example

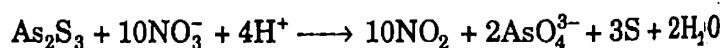


$\text{As}^{3+}$  as well as  $\text{S}^{2-}$  have been oxidised to  $\text{AsO}_4^{3-}$  and  $\text{S}$  respectively. In such case take total change (increase or decrease) in O.N. for cross-multiplication.



Total change in O.N. of oxidised part = 10

Hence, by usual steps, balance equation is



### Basic Medium

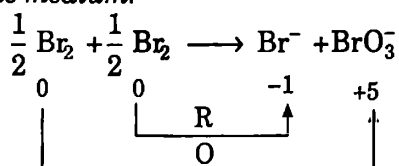
We adopt here same method as in acidic medium. Difference is only in balancing of oxygen.

— Cross-multiply by change in O.N.

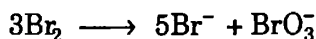
— Add  $\text{H}_2\text{O}$  on excess oxygen side.

— Add  $\text{OH}^-$  twice of  $\text{H}_2\text{O}$  on the opposite side.

**Illustration 1**  $\text{Br}_2$  disproportionates into  $\text{Br}^-$  and  $\text{BrO}_3^-$  in alkaline medium.



Cross multiplication by change in O.N. gives



(We have taken  $\frac{1}{2} \text{Br}_2$  for oxidation and reduction to balance affected atoms.)

Three O-atoms are extra on RHS, hence, add three  $\text{H}_2\text{O}$  molecules (excess O-side) on RHS, and add  $6\text{OH}^-$  on LHS

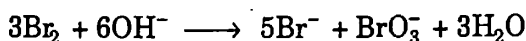
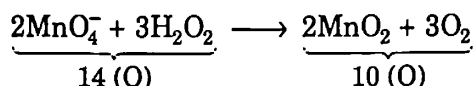
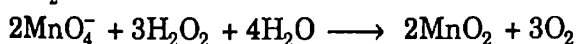


**Illustration 2**  $\text{MnO}_4^- + \text{H}_2\text{O}_2 \xrightarrow{\text{Basic}} \text{MnO}_2 + \text{O}_2$

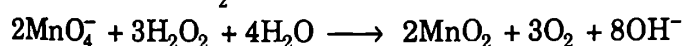
Affected atoms are balanced; by cross-multiplication



add  $\text{H}_2\text{O}$  on LHS (excess O-side)



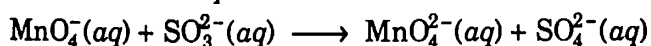
add  $\text{OH}^-$  twice of  $\text{H}_2\text{O}$  on RHS



We have proceeded in a right way, but we have not considered H due to  $\text{H}_2\text{O}_2$ . Hence, H-atoms as well as charge are not balanced. Hence, add  $6\text{H}^+$  on RHS which will neutralise  $\text{OH}^-$  forming  $6\text{H}_2\text{O}$  and thus, final result will be

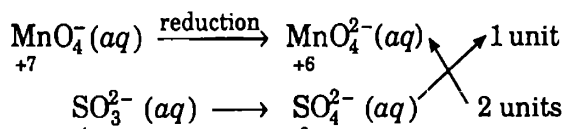


**Illustration 3** A purple solution of aqueous potassium permanganate ( $\text{KMnO}_4$ ) reacts with aqueous sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) in basic solution to yield the green manganate ion ( $\text{MnO}_4^{2-}$ ) and sulphate ion ( $\text{SO}_4^{2-}$ ). The unbalanced net ionic equation is:

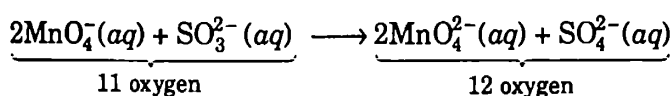


Balance the equation.

change in O.N.



Cross-multiplication followed by addition gives



Add  $\text{H}_2\text{O}$  on extra oxygen side and add twice  $\text{OH}^-$  on opposite side

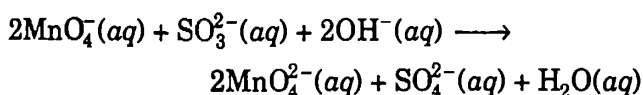
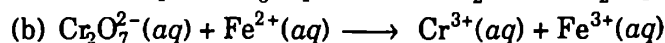
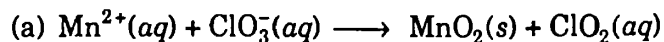
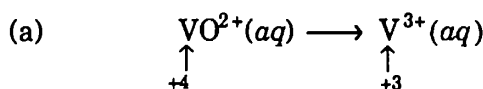
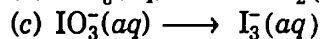
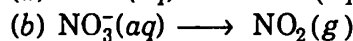
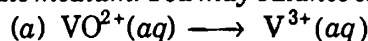


**Illustration 4** Write unbalanced half-reactions for the following net ionic equations:

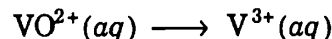


| Oxidation                                                                 | Reduction                                                                         |
|---------------------------------------------------------------------------|-----------------------------------------------------------------------------------|
| (a) $\text{Mn}^{2+}(\text{aq}) \longrightarrow \text{MnO}_2(\text{s})$    | $\text{ClO}_3^-(\text{aq}) \longrightarrow \text{ClO}_2(\text{aq})$               |
| (b) $\text{Fe}^{2+}(\text{aq}) \longrightarrow \text{Fe}^{3+}(\text{aq})$ | $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) \longrightarrow \text{Cr}^{3+}(\text{aq})$ |
| (c) $\text{Cl}_2(\text{g}) \longrightarrow \text{ClO}_3^-(\text{aq})$     | $\text{Cl}_2(\text{g}) \longrightarrow \text{Cl}^-(\text{aq})$                    |

**Illustration 5** Balance the following half-reactions in acidic medium. You may balance charges by putting electrons.



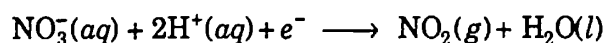
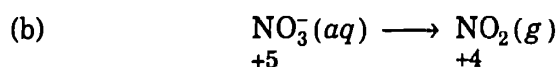
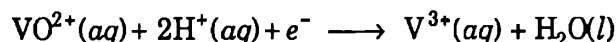
$\text{VO}^{2+}$  is reduced to  $\text{V}^{3+}$  by gain of one electron.



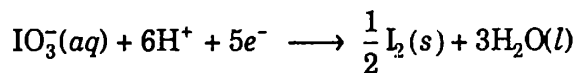
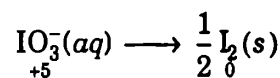
Balance O :  $\text{VO}^{2+}(\text{aq}) \longrightarrow \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

Balance H :  $\text{VO}^{2+}(\text{aq}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

Balance charge :

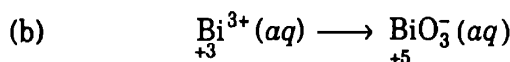
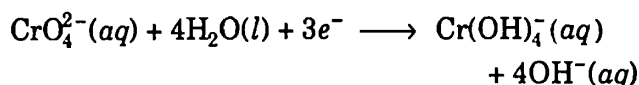
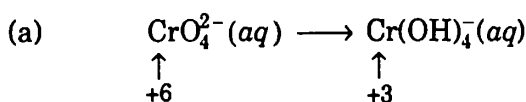
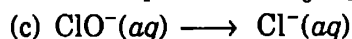
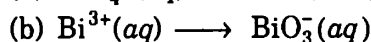
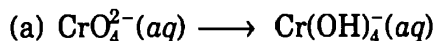


$\text{IO}_3^-(\text{aq})$  is first oxidised to  $\text{I}_2$  which dissolves in  $\text{I}^-$  forming  $\text{I}_3^-$



**Note** decrease in oxidation number = electrons added on LHS  
increase in oxidation number = electrons added on RHS

**Illustration 6** Balance the following half-reactions in a basic medium :



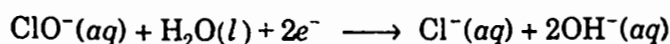
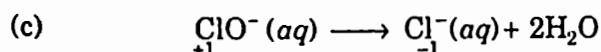
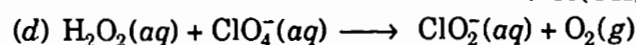
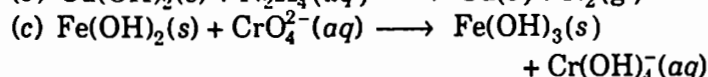
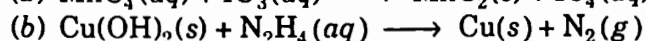
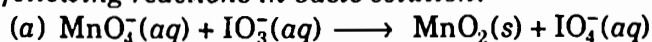
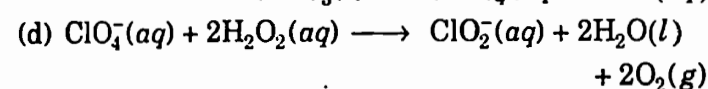
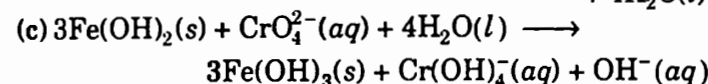
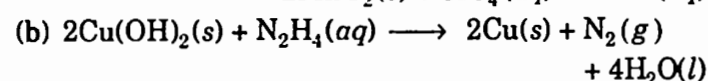
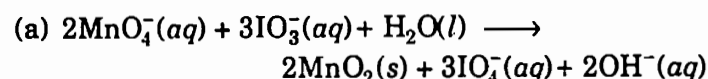


**Illustration 7** Write balanced net ionic equations for the following reactions in basic solution:



### Solution

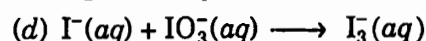
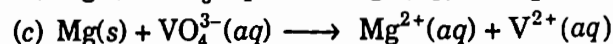
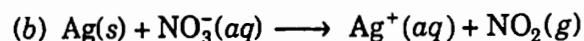


## Balanced Redox Reactions

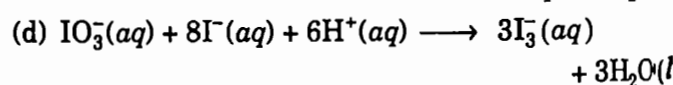
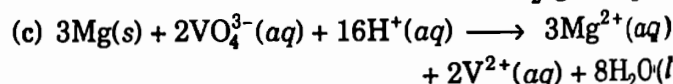
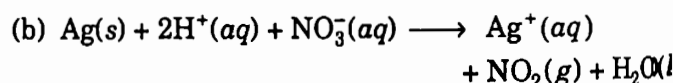
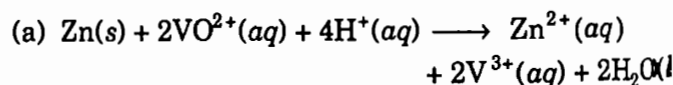
Some balanced redox reactions are in the medium specified:

- $3\text{S}_2\text{O}_4^{2-} + 2\text{CrO}_4^{2-} + 4\text{H}_2\text{O} \longrightarrow 6\text{SO}_3^{2-} + 2\text{Cr}(\text{OH})_3 + 2\text{H}^+$   
(dithionite ion)
- $3\text{CN}^- + 2\text{MnO}_4^- + \text{H}_2\text{O} \longrightarrow 2\text{MnO}_2 + 3\text{CNO}^- + 2\text{OH}^-$
- $4[\text{Fe}(\text{CN})_6]^{3-} + \text{N}_2\text{H}_4 + 4\text{OH}^- \longrightarrow 4[\text{Fe}(\text{CN})_6]^{4-} + \text{N}_2 + 4\text{H}_2\text{O}$
- $4\text{Fe}(\text{OH})_2 + \text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 4\text{Fe}(\text{OH})_3$
- $3\text{C}_2\text{H}_5\text{OH} + 4\text{MnO}_4^- \longrightarrow 3\text{CH}_3\text{COO}^- + 4\text{MnO}_2 + 4\text{H}_2\text{O} + \text{OH}^-$
- $\text{S}_2\text{O}_3^{2-} + 5\text{H}_2\text{O} + 4\text{Cl}_2 \longrightarrow 2\text{SO}_4^{2-} + 8\text{Cl}^- + 10\text{H}^+$
- $2\text{NH}_4^+ + \text{Cr}_2\text{O}_7^{2-} \longrightarrow \text{Cr}_2\text{O}_3 + \text{N}_2 + 4\text{H}_2\text{O}$
- $\text{P}_4 + 8\text{H}^+ + 20\text{NO}_3^- + 8\text{H}_2\text{O} \longrightarrow 12\text{H}_2\text{PO}_4^- + 20\text{NO}$
- $2\text{MnO}_4^- + 6\text{H}^+ + 5\text{NO}_2^- \longrightarrow 2\text{Mn}^{2+} + 5\text{NO}_3^- + 3\text{H}_2\text{O}$
- $\text{S}_8 + 12\text{OH}^- \longrightarrow 4\text{S}^{2-} + 2\text{S}_2\text{O}_3^{2-} + 6\text{H}_2\text{O}$
- $5\text{S}_2\text{O}_3^{2-} + 8\text{MnO}_4^- + 14\text{H}^+ \longrightarrow 10\text{SO}_4^{2-} + 8\text{Mn}^{2+} + 7\text{H}_2\text{O}$
- $2\text{HS}^- + 4\text{HSO}_3^- \longrightarrow 3\text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O}$
- $4\text{Fe}^{3+} + 2\text{NH}_2\text{OH} \longrightarrow 4\text{Fe}^{2+} + \text{N}_2\text{O} + 4\text{H}^+$
- $4\text{O}_2^- + 2\text{H}_2\text{O} \longrightarrow 4\text{OH}^- + 3\text{O}_2$   
(superoxide ion)
- $2[\text{Fe}(\text{CN})_6]^{4-} + \text{H}_2\text{O}_2 + 2\text{H}^+ \longrightarrow 2[\text{Fe}(\text{CN})_6]^{3-} + 2\text{H}_2\text{O}$   
(ferrocyanide ion) (ferricyanide ion)
- $\text{H}_2\text{C}_2\text{O}_4 + \text{MnO}_2 + 2\text{H}^+ \longrightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} + 2\text{CO}_2$
- $\text{IO}_3^- + 3\text{HSO}_3^- \longrightarrow \text{I}^- + 3\text{H}^+ + 3\text{SO}_4^{2-}$
- $5\text{I}^- + \text{IO}_3^- + 6\text{H}^+ \longrightarrow 3\text{H}_2\text{O} + 3\text{I}_2$
- $3\text{MnO}_4^{2-} + 2\text{H}_2\text{O} \longrightarrow \text{MnO}_2 + 2\text{MnO}_4^- + 4\text{OH}^-$

**Illustration 8** Write balanced net ionic equations for the following reactions in acidic solution:



### Solution



- $2\text{Fe}_2\text{S}_3 + 6\text{H}_2\text{O} + 3\text{O}_2 \longrightarrow 4\text{Fe}(\text{OH})_3 + 6\text{S}$
- $3\text{IBr} + 2\text{BrO}_3^- + 3\text{H}_2\text{O} \longrightarrow 3\text{IO}_3^- + 5\text{Br}^- + 6\text{H}^+$
- $\text{As}_2\text{S}_3 + 12\text{OH}^- + 14\text{H}_2\text{O}_2 \longrightarrow 2\text{AsO}_4^{3-} + 20\text{H}_2\text{O} + 3\text{SO}_4^{2-}$
- $2\text{CrI}_3 + 27\text{H}_2\text{O}_2 + 10\text{OH}^- \longrightarrow 2\text{CrO}_4^{2-} + 6\text{IO}_4^- + 32\text{H}_2\text{O}$
- $4\text{Ag} + 8\text{CN}^- + \text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 4[\text{Ag}(\text{CN})_2]^- + 4\text{OH}^-$
- $\text{B}_2\text{Cl}_4 + 6\text{OH}^- \longrightarrow 2\text{BO}_2^- + 4\text{Cl}^- + 2\text{H}_2\text{O} + \text{H}_2$
- $2\text{Ag}_2\text{S} + 8\text{CN}^- + \text{O}_2 + \text{H}_2\text{O} \longrightarrow 4[\text{Ag}(\text{CN})_2]^- + 2\text{S} + 4\text{OH}^-$
- $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{Fe}^{2+} \longrightarrow 2\text{H}_2\text{O} + 2\text{Fe}^{3+}$
- $\text{CrO} + 2\text{ClO}^- + 2\text{OH}^- \longrightarrow \text{CrO}_4^{2-} + 2\text{Cl}^- + \text{H}_2\text{O}$
- $5\text{As}_2\text{S}_3 + 4\text{MnO}_4^- + 9\text{H}_2\text{O} + 12\text{H}^+ \longrightarrow 10\text{H}_3\text{AsO}_4 + 15\text{S} + 4\text{Mn}^{2+}$
- $\text{O}_3 + 2\text{I}^- + \text{H}_2\text{O} \longrightarrow \text{O}_2 + \text{I}_2 + 2\text{OH}^-$
- $\text{S}_2\text{O}_3^{2-} + 4\text{Cl}_2 + 5\text{H}_2\text{O} \longrightarrow 2\text{HSO}_4^- + 8\text{H}^+ + 8\text{Cl}^-$
- $2\text{CN}^- + 5\text{ClO}^- + \text{H}_2\text{O} \longrightarrow 2\text{HCO}_3^- + 5\text{Cl}^- + \text{N}_2$
- $6\text{ClO}_2 + 6\text{OH}^- \longrightarrow 5\text{ClO}_3^- + \text{Cl}^- + 3\text{H}_2\text{O}$
- $4\text{Zn} + 10\text{H}^+ + \text{NO}_3^- \longrightarrow 4\text{Zn}^{2+} + \text{NH}_4^+ + 3\text{H}_2\text{O}$
- $4\text{Zn} + 10\text{H}^+ + 2\text{NO}_3^- \longrightarrow 4\text{Zn}^{2+} + \text{N}_2\text{O} + 5\text{H}_2\text{O}$
- $2\text{MnO} + 5\text{PbO}_2 + 8\text{H}^+ \longrightarrow 2\text{MnO}_4^- + 5\text{Pb}^{2+} + 4\text{H}_2\text{O}$
- $2\text{OCl}^- + 2\text{OH}^- + \text{Bi}_2\text{O}_3 \longrightarrow 2\text{BiO}_3^- + \text{H}_2\text{O} + 2\text{Cl}^-$
- $8\text{Al} + 3\text{OH}^- + 3\text{HSO}_4^- \longrightarrow 4\text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} + 3\text{S}^{2-}$
- $4\text{Ag} + 8\text{CN}^- + \text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 4[\text{Ag}(\text{CN})_2]^- + 4\text{OH}^-$
- $\text{P}_4 + 4\text{OH}^- + 2\text{H}_2\text{O} \longrightarrow 2\text{PH}_3 + 2\text{HPO}_3^{2-}$

## Target Practice 3

Balance the following redox reactions

1.  $\text{SO}_2(g) + \text{HNO}_2(aq) \longrightarrow \text{H}_2\text{SO}_4(aq) + \text{NO}(g)$
2.  $\text{Al}(s) + \text{H}_2\text{SO}_4(aq) \longrightarrow \text{Al}_2(\text{SO}_4)_3(aq) + \text{H}_2(g)$
3.  $\text{Au}^{3+}(aq) + \text{I}^-(aq) \longrightarrow \text{Au}(s) + \text{I}_2(s)$
4.  $\text{S}^{2-}(aq) + \text{I}_2(s) \longrightarrow \text{SO}_4^{2-}(aq) + \text{I}^-(aq)$
5.  $\text{H}_2\text{O}_2(aq) + \text{ClO}_4^-(aq) \longrightarrow \text{O}_2(g) + \text{ClO}_2^-(aq)$

6.  $\text{Br}_2(aq) + \text{OH}^-(aq) \longrightarrow \text{Br}^-(aq) + \text{BrO}_3^-(aq)$
7.  $\text{Mn}(s) + \text{HNO}_3(aq) \longrightarrow \text{Mn}^{2+}(aq) + \text{NO}_2(g)$
8.  $\text{I}_2(s) + \text{OCl}^-(aq) \longrightarrow \text{IO}_3^-(aq) + \text{Cl}^-(aq)$
9.  $\text{Cr}_2\text{O}_7^{2-}(aq) + \text{HNO}_2(aq) \longrightarrow \text{Cr}^{3+}(aq) + \text{NO}_3^-(aq)$
10.  $\text{CrO}_4^{2-}(aq) + \text{S}^{2-}(aq) \longrightarrow \text{Cr}(\text{OH})_3(s) + \text{S}(s)$

### Answers

1.  $\text{SO}_2(g) + 2\text{HNO}_2(aq) \longrightarrow \text{H}_2\text{SO}_4(aq) + 2\text{NO}(g)$
2.  $2\text{Al}(s) + 3\text{H}_2\text{SO}_4(aq) \longrightarrow \text{Al}_2(\text{SO}_4)_3(aq) + 3\text{H}_2(g)$
3.  $2\text{Au}^{3+}(aq) + 6\text{I}^-(aq) \longrightarrow 2\text{Au}(s) + 3\text{I}_2(s)$
4.  $\text{S}^{2-}(aq) + 4\text{I}_2(s) + 4\text{H}_2\text{O}(l) \longrightarrow 8\text{I}^-(aq) + \text{SO}_4^{2-}(aq) + 8\text{H}^+(aq)$
5.  $2\text{H}_2\text{O}_2(aq) + \text{ClO}_4^-(aq) \longrightarrow 2\text{O}_2(g) + \text{ClO}_2^-(aq) + 2\text{H}_2\text{O}(l)$
6.  $3\text{Br}_2(aq) + 6\text{OH}^-(aq) \longrightarrow 5\text{Br}^-(aq) + \text{BrO}_3^-(aq) + 3\text{H}_2\text{O}(l)$

7.  $\text{Mn}(s) + 2\text{NO}_3^-(aq) + 4\text{H}^+(aq) \longrightarrow \text{Mn}^{2+}(aq) + 2\text{NO}_2(g) + 2\text{H}_2\text{O}$
8.  $\text{I}_2(s) + 5\text{OCl}^-(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{IO}_3^-(aq) + 5\text{Cl}^-(aq) + 2\text{H}^+(aq)$
9.  $\text{Cr}_2\text{O}_7^{2-}(aq) + 6\text{HNO}_2(aq) + 8\text{H}^+(aq) \longrightarrow 2\text{Cr}^{3+}(aq) + 6\text{NO}_3^-(aq) + 4\text{H}_2\text{O}(l)$
10.  $2\text{CrO}_4^{2-}(aq) + 3\text{S}^{2-}(aq) + 8\text{H}_2\text{O}(l) \longrightarrow 2\text{Cr}(\text{OH})_3(s) + 3\text{S}(s) + 10\text{OH}^-(aq)$

## Equivalent Weights

In unit 1, detailed study of equivalent weight has been given. To determine number of equivalents or equivalent weight we can compare the molecular weight to

$$\equiv 1 \text{ g H} = 1 \text{ mol of H}^+$$

$$\equiv 17 \text{ g OH}^- = 1 \text{ mol of OH}^-$$

$$\equiv 12 \text{ g C}$$

$$\equiv 35.5 \text{ g Cl}$$

$$\equiv 8 \text{ g O}$$

## Equivalent Weight of Non-metals

Equivalent weight of non-metals can be determined by

### (i) Direct combination with hydrogen

| Non-metal       | Compound with hydrogen | Mass of hydrogen | Equivalent Mass = of non-metal combining with 1 g H |
|-----------------|------------------------|------------------|-----------------------------------------------------|
| (a) Carbon-12   | $\text{CH}_4$          | 4 g              | 3 g                                                 |
| (b) Boron-10.8  | $\text{BH}_3$          | 3 g              | 3.6 g                                               |
| (c) Nitrogen-14 | $\text{NH}_3$          | 3 g              | 4.66 g                                              |

### (ii) Conversion into oxide

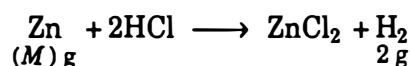
| Non-metal   | Compound with oxygen | Oxygen combined | Mass of non-metal combining with 8 g oxygen = equivalent weight |
|-------------|----------------------|-----------------|-----------------------------------------------------------------|
| Carbon-12   | $\text{CO}_2$        | 32 g            | $\frac{12}{32} \times 8 = 3 \text{ g}$                          |
| Nitrogen-14 | $\text{NO}$          | 16 g            | $\frac{14}{16} \times 8 = 7 \text{ g}$                          |
| Nitrogen-14 | $\text{NO}_2$        | 32 g            | $\frac{14}{32} \times 8 = 3.5 \text{ g}$                        |
| Nitrogen-14 | $\text{N}_2\text{O}$ | 16 g            | $\frac{28}{16} \times 8 = 14 \text{ g}$                         |

In the above example, it is clear that depending upon the compound formed **nitrogen** has different equivalent weight.

## Equivalent Weight of Metals

### 1. Replacement of hydrogen from acids

We compare the mass of metal that displaces 1 g ( $\text{H}_2$ )

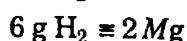
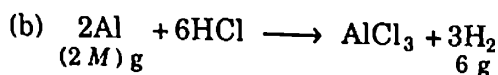


$$\text{H}_2 \equiv \text{Zn}$$

$$2 \text{ g H}_2 \equiv M \text{ g metal}$$

$$\therefore 1 \text{ g H}_2 \equiv \frac{M}{2}$$

$$\therefore \text{Equivalent weight of Zn} = \frac{\text{Atomic weight}}{2}$$

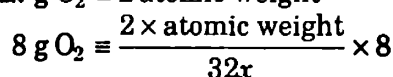
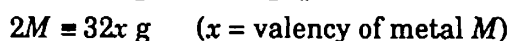
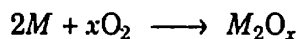


$$1 \text{ g H}_2 \equiv \frac{2M}{6} = \frac{M}{3}$$

$$\therefore \text{Equivalent weight of Al} = \frac{\text{atomic weight}}{3}$$

## 2. Conversion of Metals into Oxide

We compare the mass of metal that combines with 8 g oxygen.



$$= \frac{\text{atomic weight}}{2x}$$

We can also calculate equivalent weight by taking weight of metal and metal oxide.

Let weight of metal =  $a$  g

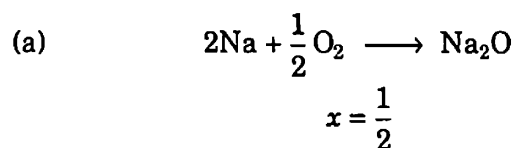
Weight of metal oxide =  $b$  g

Oxygen combined =  $(b - a)$  g

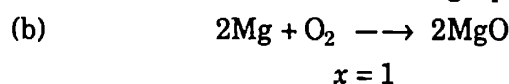
$(b - a)$  g oxygen combined with =  $a$  g metal

$$\therefore 8 \text{ g oxygen combined with} = \frac{a}{b - a} \times 8 \text{ g}$$

$$\therefore \text{Equivalent weight of metal} = \frac{8a}{(b - a)}$$



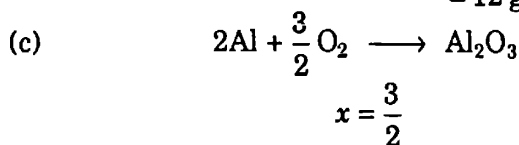
Equivalent weight of sodium = atomic weight  
= 23 g equivalent<sup>-1</sup>



Equivalent weight of magnesium =  $\frac{\text{atomic weight}}{2}$

$$= \frac{24}{2}$$

$$= 12 \text{ g equivalent}^{-1}$$



Equivalent weight of aluminium =  $\frac{\text{atomic weight}}{3}$

$$= \frac{27}{3}$$

$$= 9 \text{ g equivalent}^{-1}$$

## 3. Conversion of Metals into Chlorides

We compare the mass of metal that combines with 35.5 g of chlorine.

Let mass of metal =  $a$  g

Mass of metal chloride =  $b$  g

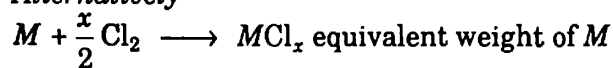
Chlorine combined =  $(b - a)$  g

$(b - a)$  g chlorine =  $a$  g metal

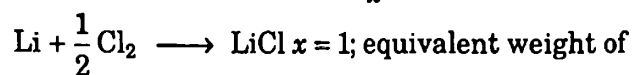
$$\therefore 35.5 \text{ g chlorine} = \frac{a}{(b - a)} \times 35.5 \text{ g}$$

$$\therefore \text{Equivalent weight of metal} = \frac{35.5a}{(b - a)}$$

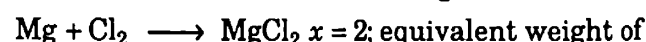
Alternatively



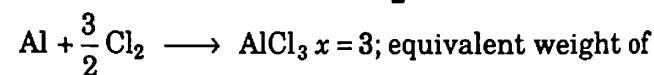
$$= \frac{\text{atomic weight}}{x}$$



Li = atomic weight



$$\text{Mg} = \frac{\text{atomic weight}}{2}$$



$$\text{Al} = \frac{\text{atomic weight}}{3}$$

**Illustration 1** (a) 0.24 g of magnesium combined with oxygen forming 0.40 g magnesium oxide. Derive equivalent weight of magnesium.

(b) 0.27 g aluminium combined with hydrogen forming 0.30 g aluminium hydride. Derive equivalent weight of aluminium.

(c) 1.95 g of platinum forms 3.37 g of chlorides on reaction with chlorine. Derive equivalent weight of platinum.

**Solution** (a) Mass of magnesium = 0.24 g

Mass of magnesium oxide = 0.40 g

Oxygen combined = 0.40 - 0.24

$$= 0.16 \text{ g}$$

0.16 g oxygen combined with = 0.24 g magnesium

$$\therefore 8 \text{ g oxygen combined with} = \frac{0.24}{0.16} \times 8 = 12 \text{ g}$$

$\therefore$  Equivalent weight of magnesium

$$= 12 \text{ g equivalent}^{-1}$$

(b) Mass of aluminium = 0.27 g

Mass of aluminium hydride = 0.30 g

Hydrogen combined = 0.03 g

0.03 g hydrogen combines with = 0.27 g aluminium

$$\therefore 1 \text{ g hydrogen combines with} = \frac{0.27}{0.03} \times 1 \text{ g} = 9 \text{ g}$$

$$\therefore \text{Equivalent weight of aluminium} \\ = 9 \text{ g equivalent}^{-1}$$

$$(c) \text{ Mass of platinum} = 1.95 \text{ g}$$

$$\text{Mass of platinum chloride} = 3.37 \text{ g}$$

$$\text{Mass of chlorine combined} = 3.37 - 1.95 \\ = 1.42 \text{ g}$$

$$1.42 \text{ g chlorine combines with} = 1.95 \text{ g platinum}$$

$$\therefore 35.5 \text{ g chlorine combines with} = \frac{1.95 \times 35.5}{1.42} \\ = \frac{195}{4} = 48.75 \text{ g}$$

$$\therefore \text{Equivalent weight of platinum} \\ = 48.75 \text{ g equivalent}^{-1}$$

## Equivalent Weight of Acids and Bases

### In a Neutralisation Reaction

We compare molecular weight w.r.t. ionisable  $\text{H}^+$  (in acids, called basicity) or  $\text{OH}^-$  (in bases, called acidity).

|                                                                                             | <i>M</i>  |      |
|---------------------------------------------------------------------------------------------|-----------|------|
| $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$                                    | $E = M/1$ | 36.5 |
| $\text{H}_3\text{PO}_2 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_2^-$             | $E = M/1$ | 66.0 |
| $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$                           | $E = M/1$ | 61.0 |
| $\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{H}^+ + \text{SO}_4^{2-}$                   | $E = M/2$ | 98.0 |
| $\text{H}_3\text{PO}_3 \rightleftharpoons 2\text{H}^+ + \text{HPO}_3^{2-}$                  | $E = M/2$ | 82.0 |
| $\text{H}_2\text{C}_2\text{O}_4 \rightleftharpoons 2\text{H}^+ + \text{C}_2\text{O}_4^{2-}$ | $E = M/2$ | 90.0 |
| $\text{H}_3\text{PO}_4 \rightleftharpoons 3\text{H}^+ + \text{PO}_4^{3-}$                   | $E = M/3$ | 98.0 |
| $\text{NaOH} \rightleftharpoons \text{Na}^+ + \text{OH}^-$                                  | $E = M$   | 40.0 |
| $\text{Ca(OH)}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$                          | $E = M/2$ | 74.0 |
| $\text{Al(OH)}_3 \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^-$                          | $E = M/3$ | 78.0 |

**Facts:** It must be noted that equivalent weight is not a definite property but varies reaction to reaction.

$\text{H}_3\text{PO}_4$  is a tribasic acid. But in the following reaction only two  $\text{H}^+$  ions have been neutralised:

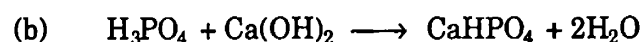
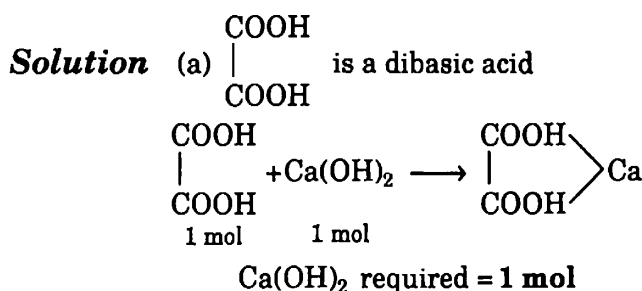
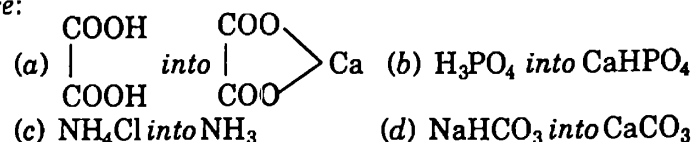


Hence, equivalent weight of  $\text{H}_3\text{PO}_4 = M/2 = 49$  and if reaction proceeds completely



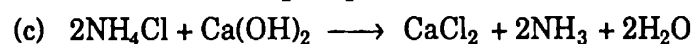
$$\text{Equivalent weight} = \frac{M}{3} = \frac{98}{3} = 32.66$$

**Illustration 1** Calculate moles of  $\text{Ca(OH)}_2$  required to carry out following conversion taking one mole in each case:



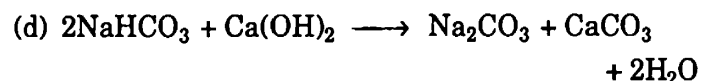
1 mol of  $\text{H}_3\text{PO}_4 \equiv 2\text{H}^+$  neutralised by 1 mol of  $\text{Ca(OH)}_2$

$\text{Ca(OH)}_2 \text{ required} = 1 \text{ mol}$



2 mol  $\text{NH}_4\text{Cl} \equiv 1 \text{ mol } \text{Ca(OH)}_2$

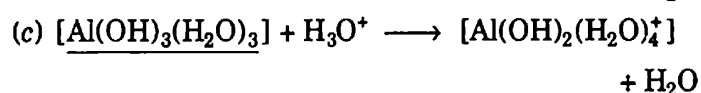
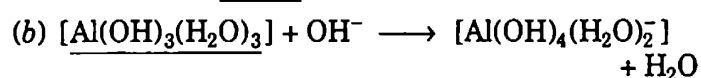
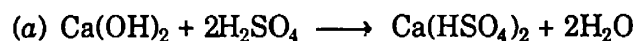
1 mol  $\text{NH}_4\text{Cl} \equiv 0.5 \text{ mol } \text{Ca(OH)}_2$



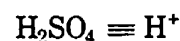
2 mol  $\text{NaHCO}_3 \equiv 1 \text{ mol } \text{Ca(OH)}_2$

1 mol  $\text{NaHCO}_3 \equiv 0.5 \text{ mol } \text{Ca(OH)}_2$

**Illustration 2** Calculate equivalent weight of the underlined:



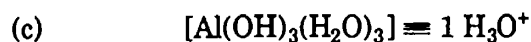
**Solution** (a)  $\text{H}_2\text{SO}_4$  changes to  $\text{HSO}_4^-$  i.e., only one  $\text{H}^+$  reacts



$\therefore$  Equivalent weight of  $\text{H}_2\text{SO}_4 = \text{molecular weight} = 98$



$\therefore$  equivalent weight = molecular weight



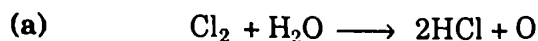
$\therefore$  equivalent weight = molecular weight

### In a Redox Reaction

Depending on the nature of products of a redox reaction, equivalent weight is determined.

- Compare molecular weight w.r.t. 8 g (O) if oxygen is gained or lost. For this convert every (O) atom gained or lost into **two parts** :

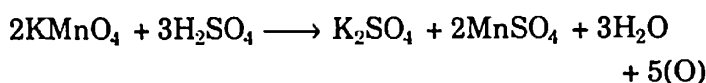




$$\begin{aligned}\therefore \quad \text{Cl}_2 &\equiv 1 (\text{O}) \text{ taking weight as } 16 \\ &\equiv 2 (\text{O}) \text{ taking weight as } 8 \\ \frac{\text{Cl}_2}{2} &\equiv 1 (\text{O})\end{aligned}$$

$$\therefore \text{Equivalent weight of } \text{Cl}_2 = \frac{M}{2}$$

(b)  $\text{KMnO}_4$  in acidic medium loses 2.5 oxygen atoms

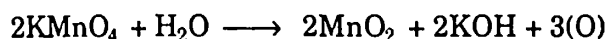


Thus,  $\text{KMnO}_4 \equiv 2.5 (\text{O})$  atoms taking weight as 16  
 $\equiv 5 (\text{O})$  atoms taking weight as 8

$$\frac{\text{KMnO}_4}{5} \equiv 1 (\text{O})$$

$$\therefore \text{Eq. wt. of } \text{KMnO}_4 \text{ in acidic medium} = \frac{M}{5}$$

(c)  $\text{KMnO}_4$  in basic and neutral medium loses 1.5 oxygen atoms

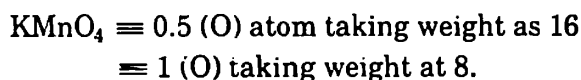


Thus,  $\text{KMnO}_4 \equiv 1.5 (\text{O})$  atoms taking weight as 16  
 $\equiv 3 (\text{O})$  atoms taking weight as 8

$$\frac{\text{KMnO}_4}{3} \equiv 1 (\text{O})$$

$$\therefore \text{Eq. wt. of } \text{KMnO}_4 \text{ in basic medium} = \frac{M}{3}$$

(d)  $\text{KMnO}_4$  in strongly alkaline medium loses 0.5 oxygen atom



$$\therefore \text{Eq. wt. of } \text{KMnO}_4 \text{ in neutral medium} = \frac{M}{1}$$

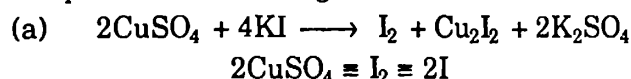
Thus, eq. wt. is not a definite property. It also depends on medium. Eq. wt. of  $\text{KMnO}_4$  as we shall above is quite different in three media, acidic, basic and neutral. (mol. wt. = 158)

$$\text{Acidic} = \frac{M}{5} = 31.6$$

$$\text{Basic and neutral} = \frac{M}{3} = 52.66$$

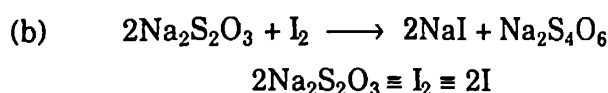
$$\text{Strongly alkaline} = \frac{M}{1} = 158.0$$

- In certain cases  $\text{I}_2$  is formed or used. In such cases compare molecular weight with one I atom.

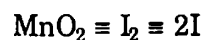
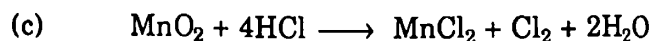


$$\therefore \text{I} \equiv \text{CuSO}_4$$

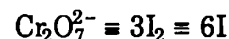
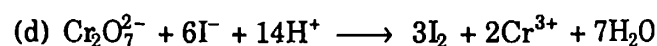
$$\therefore \text{Eq. wt. of } \text{CuSO}_4 = M$$



$$\therefore \text{Eq. wt. of } \text{Na}_2\text{S}_2\text{O}_3 = M$$



$$\therefore \text{Eq. wt. of } \text{MnO}_2 = \frac{M}{2}$$



$$\therefore \text{Eq. wt. of } \text{Cr}_2\text{O}_7^{2-} = \frac{M}{6}$$

## DEEP Focus

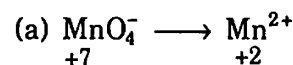
- Easiest method of determination of eq. wt. in a redox reaction is by

$$\text{Eq. wt.} = \frac{\text{formula weight (stoichiometric)}}{\text{change in O.N. or electron exchanged}}$$

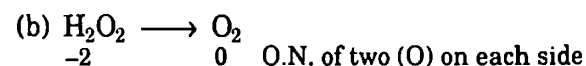
We have used the term “**formula weight**” to simplify the definition. While using this term, check

- affected atoms are balanced
- take total O.N. of the affected atom of each side.

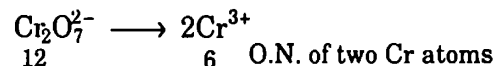
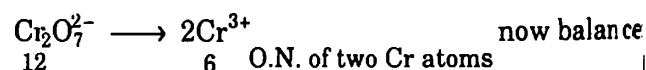
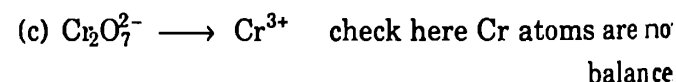
## Illustration 1



$$\text{Eq. wt.} = \frac{\text{mol. wt. of one unit of } \text{MnO}_4^-}{5}$$

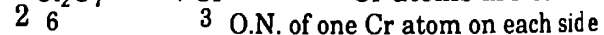
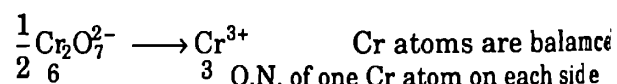
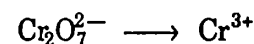


$$\text{Eq. wt.} = \frac{M}{2}$$



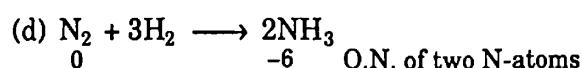
$$\text{Eq. wt.} = \frac{M}{6}$$

We can also take it as follows :



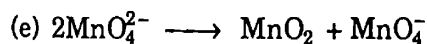
$$\text{Eq. wt.} = \frac{\left(\frac{1}{2}\right) \text{ formula weight}}{3} = \frac{M/2}{3} = \frac{M}{6}$$

(half molecule is on LHS)



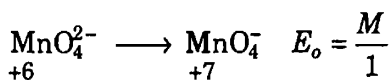
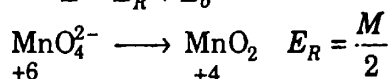
$$\text{Eq. wt. of } \text{NH}_3 = \frac{2 \text{ formula weight of } \text{NH}_3}{6} = \frac{M}{3}$$

$$\text{Eq. wt. of } \text{N}_2 = \frac{M}{6} = \frac{28}{6} = \frac{14}{3}$$

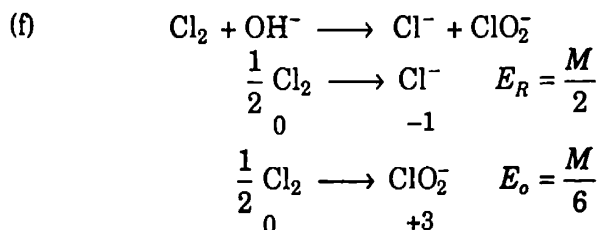


$\text{MnO}_4^{2-}$  disproportionates to  $\text{MnO}_2$  and  $\text{MnO}_4^-$ . If  $E_R$  is the equivalent weight in the reduction half-reaction and  $E_o$  is the equivalent weight in the oxidation half-reaction then net equivalent weight  $E$

$$E = E_R + E_o$$



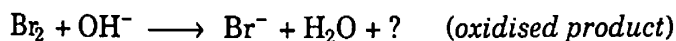
$$E(\text{net}) = \frac{M}{2} + \frac{M}{1} = 1.5 M$$



(0.5 mol of  $\text{Cl}_2$  is used in each half-reaction)

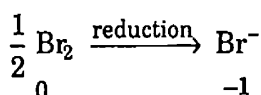
$$E(\text{net}) = \frac{M}{2} + \frac{M}{6} = \frac{2}{3} M$$

**Illustration 2** Equivalent weight of  $\text{Br}_2$  is 96 in the following disproportionation reaction:



Identify the oxidised product. ( $\text{Br} = 80$ )

**Solution** Molar mass of  $\text{Br}_2 = 160 \text{ g mol}^{-1}$

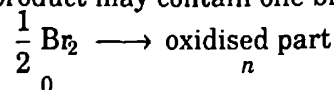


$$\begin{aligned} \text{Equivalent weight of } \text{Br}_2 &= \frac{\text{formula weight}}{1} \\ &= \frac{160}{2} = 80 \end{aligned}$$

Net equivalent weight (given) = 96

$\therefore$  Equivalent weight of  $\text{Br}_2$  in oxidation process  
 $= 96 - 80 = 16$

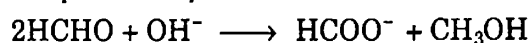
Let oxidised product may contain one bromine



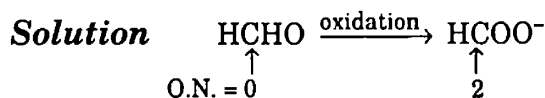
$$\begin{aligned} \text{Equivalent weight} &= 16 = \frac{80}{\text{change in O.N.}} \\ &= \frac{80}{n} \\ n &= \frac{80}{16} = 5 \end{aligned}$$

Thus, oxidation number of Br in oxidised part is +5. It is  $\text{BrO}_3^-$

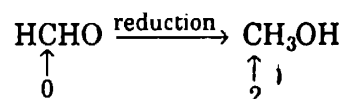
**Illustration 3**  $\text{HCHO}$  disproportionates to  $\text{HCOO}^-$  and  $\text{CH}_3\text{OH}$  in presence of  $\text{OH}^-$  (Cannizzaro reaction).



Calculate equivalent weight of  $\text{HCHO}$ .



$$\begin{aligned} \text{Equivalent weight of HCHO} &= \frac{\text{molecular weight}}{\text{change in O.N.}} \\ &= \frac{M}{2} \end{aligned}$$



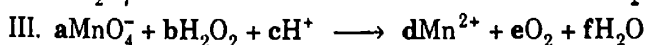
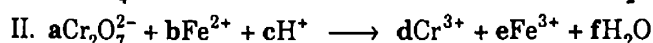
$$\text{Equivalent weight of HCHO} = \frac{M}{2}$$

In a disproportionation reaction, net equivalent weight = sum of equivalent weights of oxidation and reduction reactions

$$= \frac{M}{2} + \frac{M}{2} = M = 30$$

## Target Practice 4

1. In the following redox reactions, write values of a to f



|     | a | b | c | d | e | f |
|-----|---|---|---|---|---|---|
| I   |   |   |   |   |   |   |
| II  |   |   |   |   |   |   |
| III |   |   |   |   |   |   |

2. Molecular weight of  $\text{KMnO}_4$  is 158.  $\text{KMnO}_4$  can be reduced to  $\text{MnSO}_4$ ,  $\text{K}_2\text{MnO}_4$  and  $\text{MnO}_2$  and equivalent weight of  $\text{KMnO}_4$  comes out to be 158, 52.66, 31.6. Match the equivalent weights with compounds formed by reduction.

| Equivalent weight of $\text{KMnO}_4$ | Compound formed |
|--------------------------------------|-----------------|
| 158                                  | .....           |
| 52.66                                | .....           |
| 31.6                                 | .....           |

3.  $\text{MnO}_4^-$  is an oxidant for  $\text{Fe}^{2+}$ ,  $\text{C}_2\text{O}_4^{2-}$  etc. Mention moles of  $\text{MnO}_4^-$  required by 1 mol each of

|                      | $\text{MnO}_4^-$ required |
|----------------------|---------------------------|
| (a) Ferrous oxalate  | .....                     |
| (b) Ferric sulphate  | .....                     |
| (c) Ferrous chloride | .....                     |

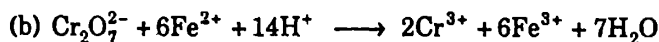
## 4. Write half reactions using electrons

(a)



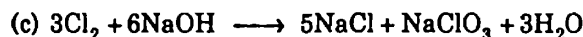
Oxidation .....

Reduction .....



Oxidation .....

Reduction .....



Oxidation .....

Reduction .....

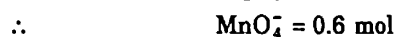
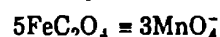
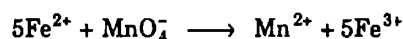
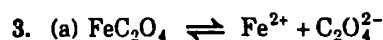
5.  $\text{KHCO}_3$  and  $\text{KHC}_2\text{O}_4$  can be estimated by base or/and  $\text{MnO}_4^-$ . Derive equivalent weight

|                          | Using base | Using $\text{MnO}_4^-$ |
|--------------------------|------------|------------------------|
| $\text{KHCO}_3$          | .....      | .....                  |
| $\text{KHC}_2\text{O}_4$ | .....      | .....                  |

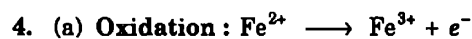
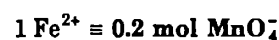
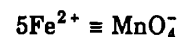
## Answers

| 1.  | a | b | c  | d | e | f |
|-----|---|---|----|---|---|---|
| I   | 1 | 5 | 8  | 1 | 5 | 4 |
| II  | 1 | 6 | 14 | 2 | 6 | 7 |
| III | 2 | 5 | 6  | 2 | 5 | 8 |

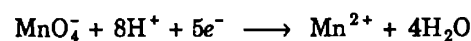
| 2. | Equivalent weight | Compound formed          |
|----|-------------------|--------------------------|
|    | 158               | $\text{K}_2\text{MnO}_4$ |
|    | 52.66             | $\text{MnO}_2$           |
|    | 31.6              | $\text{MnSO}_4$          |



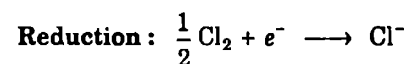
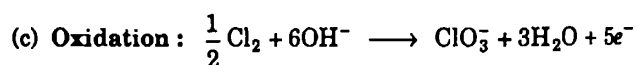
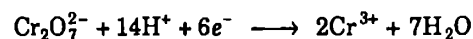
(b) Ferric sulphate  $\text{Fe}_2(\text{SO}_4)_3$  is already has iron in +3 state.  
Hence, no further oxidation by  $\text{MnO}_4^-$



Reduction :



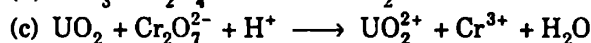
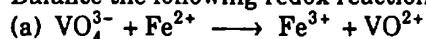
Reduction :



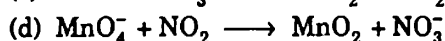
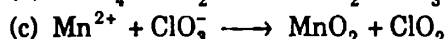
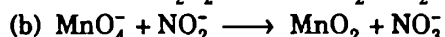
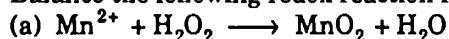
| 5. | Compound                 | Using base | Using $\text{MnO}_4^-$ |
|----|--------------------------|------------|------------------------|
|    | $\text{KHCO}_3$          | $E = M$    | cannot be used         |
|    | $\text{KHC}_2\text{O}_4$ | $E = M$    | $E = \frac{M}{2}$      |

## Practice Exercise 2

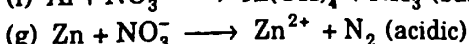
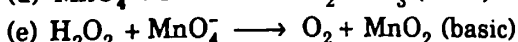
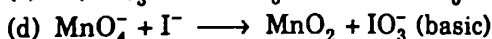
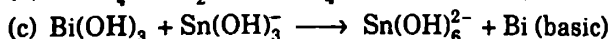
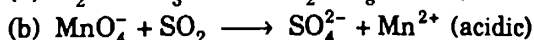
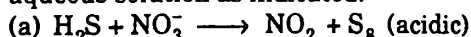
## 1. Balance the following redox reactions in acidic solution:



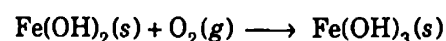
## 2. Balance the following redox reaction in basic medium:



## 3. Balance the following redox reactions in acidic or basic aqueous solution as indicated:



## 4. Balance the following equation taking place in basic solution:



## 5. Write balanced redox reactions of the following:

(a)  $\text{H}_2\text{O}_2(\text{aq})$  reduces  $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$  to green coloured  $\text{Cr}^{3+}(\text{aq})$  in acidic medium.

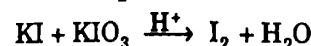
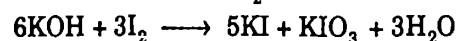
(b)  $\text{H}_2\text{O}_2(\text{aq})$  oxidises  $\text{Mn}^{2+}(\text{aq})$  to  $\text{MnO}_2$  in basic medium

(c) 4 moles of  $\text{Sn}^{2+}(\text{aq})$  reduces  $\text{IO}_4^-(\text{aq})$  to  $\text{I}^-(\text{aq})$ .

6. A given amount of  $\text{Fe}^{2+}$  is oxidised by  $x$  moles of  $\text{MnO}_4^-$  in acidic medium. Calculate number of moles of  $\text{Cr}_2\text{O}_7^{2-}$  required to oxidise same amount in  $\text{Fe}^{2+}$  in acidic medium

7.  $\text{C}_2\text{O}_4^{2-}$  can be oxidised to  $\text{CO}_2$  by  $\text{MnO}_4^-$  in acidic as well as basic medium. What is ratio of moles of  $\text{MnO}_4^-$  used per mole of  $\text{C}_2\text{O}_4^{2-}$ ?

8. How many moles of KI are oxidised by number of moles of  $\text{KIO}_3$  formed when 1 mole of  $\text{I}_2$  is boiled with excess of  $\text{KOH}$

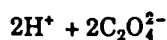


9. Calculate number of moles of  $\text{MnO}_4^-$  required to oxidise 1 mole of  $\text{Fe}(\text{HC}_2\text{O}_4)_2$  in acidic medium. How many moles of  $\text{Ca}(\text{OH})_2$  are required to react with 1 mole of  $\text{Fe}(\text{HC}_2\text{O}_4)_2$ ?
10.  $\text{H}_2\text{O}_2(aq)$  reduces  $\text{ClO}_4^-(aq)$  in acidic medium. If 1 mole of  $\text{H}_2\text{O}_2$  reduces 0.5 mole of  $\text{ClO}_4^-(aq)$ , what is the reduced species?
11.  $\text{MnO}_4^-(aq)$  can oxidise  $\text{IO}_3^-(aq)$  to  $\text{IO}_4^-(aq)$  and itself gets reduced to  $\text{MnO}_2(s)$ . Calculate number of moles of  $\text{IO}_3^-(aq)$  that can reduce 0.1 mole of  $\text{MnO}_4^-(aq)$ .
12. Calculate equivalent weight of the underlined :
- (a)  $\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2$
- (b)  $\text{NaHCO}_3 + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$
- (c)  $2\text{C}_6\text{H}_5\text{OH} + 2\text{Na} \longrightarrow 2\text{C}_6\text{H}_5\text{ONa} + \text{H}_2$
- (d)  $\begin{array}{c} \text{CH}_2\text{NH}_2 \\ | \\ \text{CH}_2\text{NH}_2 \end{array} + 2\text{HCl} \longrightarrow \begin{array}{c} \text{CH}_2\text{NH}_3^+\text{Cl}^- \\ | \\ \text{CH}_2\text{NH}_3^+\text{Cl}^- \end{array}$
- (e)  $\text{CH}=\text{CH} + 2\text{Na} \longrightarrow \text{NaC}\equiv\text{CNa} + \text{H}_2$
13. Mercuric oxide,  $\text{HgO}$ , can be analysed by reaction with iodide and then titration with an acid:
- $$\text{HgO} + 4\text{I}^- \longrightarrow \text{HgI}_4^{2-} + 2\text{OH}^-$$
- What is its equivalent weight?
14. Calculate the equivalent weight of the following substances as acids or bases:
- (a)  $\text{KH}(\text{IO}_3)_2$  (b)  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$   
 (c)  $\text{Al}(\text{OH})_3$  (d)  $\text{SO}_2(\text{OH})_2$   
 (e)  $\text{PO}(\text{OH})_3$  (f)  $\text{Zn}(\text{OH})_4^{2-}$
15. Calculate equivalent weight of  $\text{KHC}_2\text{O}_4$  (potassium acid oxalate)
- (a) when it is neutralised by  $\text{KOH}$ , and  
 (b) when it is oxidised by  $\text{MnO}_4^-$  in basic solution.
16. 0.24 g of a metal on heating in air forms 0.40 g of metal oxide. What is equivalent weight of metal?
17. Equivalent weight of  $\text{KMnO}_4$  in acidic medium is 31.6. What is corresponding value in basic medium?
18. Determine equivalent weight of underlined species taking its molecular weight as  $M$
- (a)  $4\text{H}_3\text{PO}_3 \xrightarrow{\Delta} 3\text{H}_3\text{PO}_4 + \text{PH}_3$   
 (b)  $2\text{H}_2\text{O}_2 \xrightarrow{\Delta} 2\text{H}_2\text{O} + \text{O}_2$   
 (c)  $\text{MnO}_2 \xrightarrow{\text{OH}^-} \text{MnO}_4^- + \text{Mn}^{2+}$   
 (d)  $2\text{H}_2\text{O} \xrightarrow{\Delta} 2\text{H}_2 + \text{O}_2$
19. Calculate the grams of one equivalent each of the following for the indicated reaction:
- (a)  $\text{FeSO}_4 \longrightarrow \text{Fe}^{3+}$  (b)  $\text{H}_2\text{S} \longrightarrow \text{S}^0$   
 (c)  $\text{H}_2\text{O}_2 \longrightarrow \text{O}_2$  (d)  $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O}$

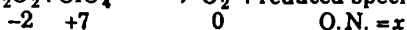
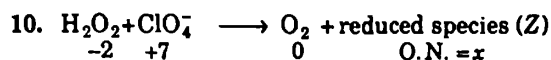
## Answers

1. (a)  $\text{VO}_4^{3-} + \text{Fe}^{2+} + 6\text{H}^+ \longrightarrow \text{Fe}^{3+} + \text{VO}^{2+} + 3\text{H}_2\text{O}$   
 (b)  $2\text{BrO}_3^- + 3\text{N}_2\text{H}_4 \longrightarrow 2\text{Br}^- + 3\text{N}_2 + 6\text{H}_2\text{O}$   
 (c)  $3\text{UO}_2 + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \longrightarrow 3\text{UO}_2^{2+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
2. (a)  $\text{Mn}^{2+} + \text{H}_2\text{O}_2 + 2\text{OH}^- \longrightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$   
 (b)  $2\text{MnO}_4^- + 3\text{NO}_2^- + \text{H}_2\text{O} \longrightarrow \text{MnO}_2 + 3\text{NO}_3^- + 2\text{OH}^-$   
 (c)  $\text{Mn}^{2+} + 2\text{ClO}_3^- \longrightarrow \text{MnO}_2 + 2\text{ClO}_2$   
 (d)  $\text{MnO}_4^- + 3\text{NO}_2 + 2\text{OH}^- \longrightarrow \text{MnO}_2 + 3\text{NO}_3^- + \text{H}_2\text{O}$
3. (a)  $8\text{H}_2\text{S} + 16\text{NO}_3^- + 16\text{H}^+ \longrightarrow 16\text{NO}_2 + \text{S}_8 + 16\text{H}_2\text{O}$   
 (b)  $2\text{MnO}_4^- + 5\text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{Mn}^{2+} + 5\text{SO}_4^{2-} + 4\text{H}^+$   
 (c)  $2\text{Bi}(\text{OH})_3 + 3\text{Sn}(\text{OH})_3 + 3\text{OH}^- \longrightarrow 2\text{Bi} + 3\text{Sn}(\text{OH})_6^{2-}$   
 (d)  $2\text{MnO}_4^- + \text{I}^- + \text{H}_2\text{O} \longrightarrow 2\text{MnO}_2 + \text{IO}_3^- + 2\text{OH}^-$   
 (e)  $3\text{H}_2\text{O}_2 + 2\text{MnO}_4^- \longrightarrow 3\text{O}_2 + 2\text{MnO}_2 + 2\text{OH}^- + 2\text{H}_2\text{O}$   
 (f)  $8\text{Al} + 3\text{NO}_3^- + 5\text{OH}^- + 18\text{H}_2\text{O} \longrightarrow 8\text{Al}(\text{OH})_4^- + 3\text{NH}_3$   
 (g)  $5\text{Zn} + 2\text{NO}_3^- + 12\text{H}^+ \longrightarrow 5\text{Zn}^{2+} + \text{N}_2 + 6\text{H}_2\text{O}$
4.  $4\text{Fe}(\text{OH})_2(s) + 2\text{H}_2\text{O}(l) + \text{O}_2(g) \longrightarrow 4\text{Fe}(\text{OH})_3(s)$
5. (a)  $\text{Cr}_2\text{O}_7^{2-} + 3\text{H}_2\text{O}_2 + 8\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 3\text{O}_2 + 7\text{H}_2\text{O}$   
 (b)  $\text{Mn}^{2+} + \text{H}_2\text{O}_2 + 2\text{OH}^- \longrightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$   
 (c)  $4\text{Sn}^{2+} + \text{IO}_4^- + 8\text{H}^+ \longrightarrow 4\text{Sn}^{4+} + \text{I}^- + 4\text{H}_2\text{O}$
6.  $6\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} \xrightarrow{\text{H}^+} 2\text{Cr}^{3+} + \text{H}_2\text{O} + 6\text{Fe}^{3+}$   
 $5\text{Fe}^{2+} + \text{MnO}_4^- \xrightarrow{\text{H}^+} \text{Mn}^{2+} + \text{H}_2\text{O} + 5\text{Fe}^{3+}$   
 $\frac{\text{mole of MnO}_4^-}{\text{mole of Cr}_2\text{O}_7^{2-}} = \frac{5}{6}, \quad \frac{x}{\text{mole of Cr}_2\text{O}_7^{2-}} = \frac{5}{6} \quad (\text{ratio of Fe}^{2+} \text{ oxidised})$   
 $\text{mole of Cr}_2\text{O}_7^{2-} = 1.2x$
7.  $5\text{C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- \xrightarrow{\text{H}^+} 10\text{CO}_2 + 2\text{Mn}^{2+}$   
 $3\text{C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- \xrightarrow{\text{OH}^-} 6\text{CO}_2 + 2\text{MnO}_2$   
 $1 \text{ C}_2\text{O}_4^{2-} \equiv \frac{2}{5} \text{ MnO}_4^- \text{ (acidic)}$   
 $1 \text{ C}_2\text{O}_4^{2-} \equiv \frac{2}{3} \text{ MnO}_4^- \text{ (basic)}$   
 ratio of mole of  $\text{MnO}_4^-$  used = 3 : 5
8. By given reaction  
 $3\text{I}_2 \equiv \text{KIO}_3$   
 $1 \text{ I}_2 = \frac{1}{3} \text{ KIO}_3 = \frac{1}{3} \text{ KI}$   
 Hence,  $\frac{1}{3}$  mol.
9.  $\text{Fe}(\text{HC}_2\text{O}_4)_2 \rightleftharpoons \text{Fe}^{2+} + 2\text{HC}_2\text{O}_4^-$   
 $\text{MnO}_4^-$  oxidises  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and  $\text{HC}_2\text{O}_4^-$  to  $\text{CO}_2$ .  
 $\text{MnO}_4^- + 5\text{Fe}^{2+} \longrightarrow 5\text{Fe}^{3+} + \text{Mn}^{2+}$   
 $2\text{MnO}_4^- + 5\text{HC}_2\text{O}_4^- \longrightarrow 10 \text{ CO}_2 + 2\text{Mn}^{2+}$   
 $5\text{Fe}^{2+} \equiv 1 \text{ MnO}_4^-$   
 $1\text{Fe}^{2+} \equiv \frac{1}{5} \text{ MnO}_4^-$   
 $5\text{HC}_2\text{O}_4^- \equiv 2\text{MnO}_4^-$   
 $2\text{HC}_2\text{O}_4^- \equiv \frac{4}{5} \text{ MnO}_4^-$   
 Total  $\text{MnO}_4^-$  required by 1 mol of  $\text{Fe}(\text{HC}_2\text{O}_4)_2$   
 $= \frac{1}{5} + \frac{4}{5} = 1 \text{ mol}$

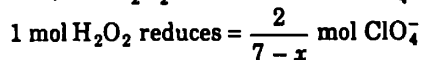
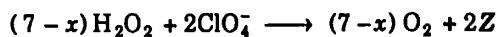
$\text{Fe}(\text{HC}_2\text{O}_4)_2$  has two acidic  $\text{H}^+$



Thus,  $\text{Ca}(\text{OH})_2$  required by 1 mol of  $\text{Fe}(\text{HC}_2\text{O}_4)_2 = 1$  mol



Balancing O.N.

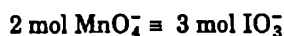
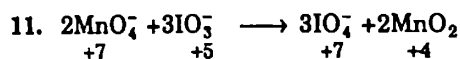


$$\frac{2}{7-x} = 0.5 \text{ mol ClO}_4^- \text{ (given)}$$

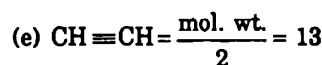
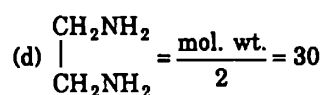
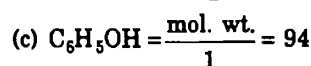
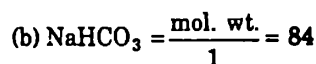
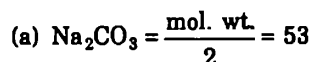
$$4 = 7 - x$$

$$x = 3$$

Oxidation number of Cl in Z is +3, Z is  $\text{ClO}_2^-$ .



12. Equivalent weight of



13.  $\text{HgO} \equiv 2\text{OH}^- \equiv 2\text{H}^+$



$$\text{Equivalent weight of HgO} = \frac{\text{molecular weight}}{2}$$

14. If  $M$  is the molecular weight and  $E$  the equivalent weight, then

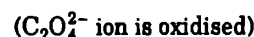
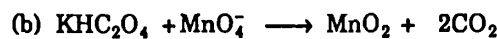
$$(a) E = M \quad (b) E = \frac{M}{3} \quad (c) E = \frac{M}{4}$$

$$(d) E = \frac{M}{2} \quad (e) E = \frac{M}{3} \quad (f) E = \frac{M}{4}$$

15. (a)  $\text{KHC}_2\text{O}_4 + \text{KOH} \longrightarrow \text{K}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O}$



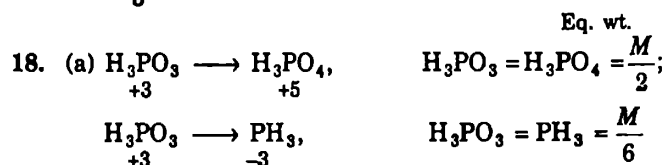
$$\text{Equivalent weight} = \frac{\text{mol. wt.}}{1} = 128$$



$$\text{Equivalent weight of KHC}_2\text{O}_4 = \frac{\text{mol. wt.}}{2} = 64$$

16. 12 g/equivalent.

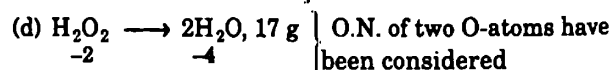
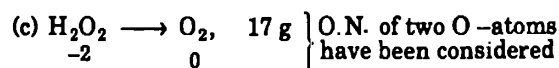
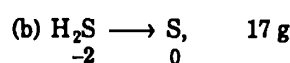
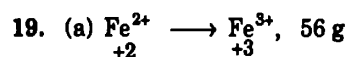
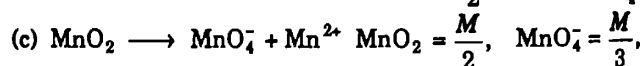
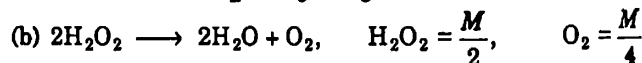
$$17. 31.6 \times \frac{5}{3} = 52.66 \text{ g / equivalent.}$$



In total reaction, equivalent weight of the species undergoing disproportionation

= sum of equivalent weight of half reactions

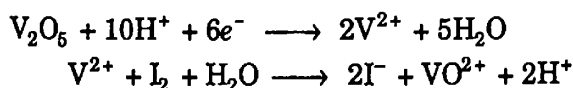
$$= \frac{M}{2} + \frac{M}{6} = \frac{2}{3} M$$



# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** If 10 g  $V_2O_5$  is dissolved in acid and reduced to  $V^{2+}$  by treatment with zinc metal, how many moles of  $I_2$  could be reduced by the resulting  $V^{2+}$  solution, as it is oxidised to  $V^{4+}$ ? ( $V = 51$ )



**Plan** On comparison of stoichiometric coefficients, we find

$$1 \text{ mol } V_2O_5 \equiv 2 \text{ mol } I_2$$

**Solution** From the above equations,

1 mol of  $V_2O_5$  is reduced to 2 mol of  $V^{2+}$

1 mol of  $V^{2+}$  reduces 1 mol of  $I_2$

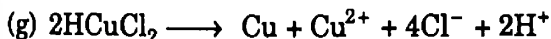
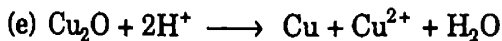
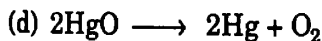
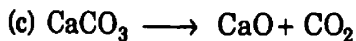
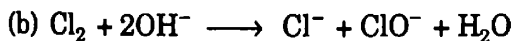
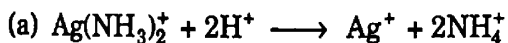
Thus, 1 mol of  $V_2O_5$  reduces 2 mol of  $I_2$

hence, 10 g of  $V_2O_5 = \left( \frac{10}{182} \text{ mol} \right)$  reduces

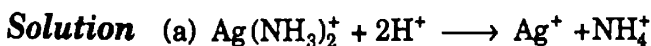
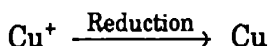
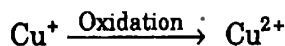
$$= 2 \times \frac{10}{182} \text{ mol } I_2$$

$$= 0.11 \text{ mol } I_2$$

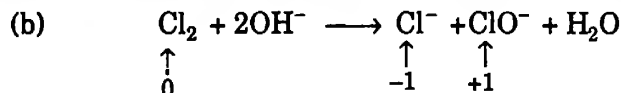
**Problem 2.** Which of the following are examples of disproportionation reactions?



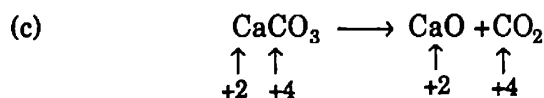
**Plan** A disproportionation reaction is that in which the same species is oxidised as well as reduced.



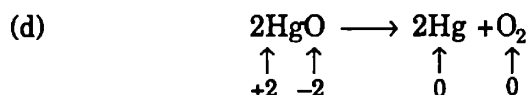
no change, neither oxidation nor reduction



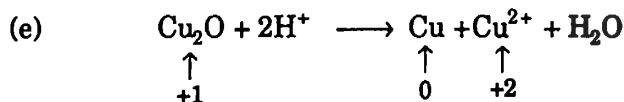
$Cl_2$  is reduced to  $Cl^-$  as well as oxidised to  $ClO^-$  hence,  $Cl_2$  undergoes disproportionation.



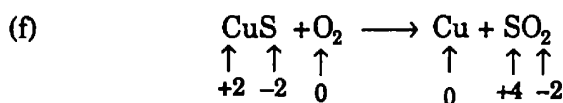
no change



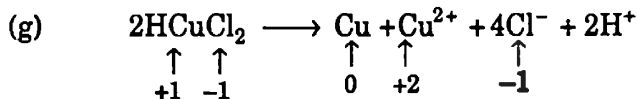
There is oxidation of O and reduction of Hg. It is a redox reaction but not disproportionation.



There is oxidation of  $Cu^+$  to  $Cu^{2+}$  as well as reduction to Cu, hence,  $Cu^+$  disproportionates.



This is also a redox but not disproportionation reaction.



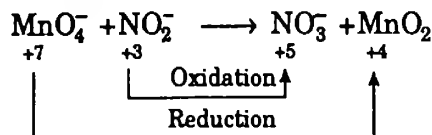
$Cu^+$  disproportionates to  $Cu^{2+}$  and Cu.

**Problem 3.**  $MnO_4^-$  can oxidise  $NO_2^-$  to  $NO_3^-$  in basic medium. How many moles of  $NO_2^-$  are oxidised by 1 mole of  $MnO_4^-$ ?

**Plan** On comparison of change of oxidation number,

$$2 \text{ mol of } MnO_4^- \equiv 3 \text{ mol of } NO_2^-$$

**Solution**  $NO_2^-$  is oxidised to  $NO_3^-$  by  $MnO_4^-$  (in basic medium) which is reduced to  $MnO_2$

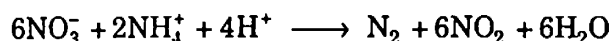


Thus,  $\text{MnO}_4^- \longrightarrow \text{MnO}_2$  oxidation number decreases by 3-units

$\text{NO}_2^- \longrightarrow \text{NO}_3^-$  oxidation number increases by 2-units

$$\begin{aligned}\text{Thus,} \quad 2\text{MnO}_4^- &\equiv 3\text{NO}_2^- \\ 1\text{MnO}_4^- &\equiv \frac{3}{2}\text{NO}_2^- \\ &= 1.5\text{ mol NO}_2^-\end{aligned}$$

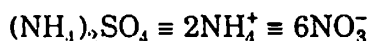
**Problem 4.** In certain laboratory procedures it is necessary to remove  $\text{NH}_4^+$  ions from solution by heating with  $\text{HNO}_3$ . Write balanced ionic reaction if  $\text{NH}_4^+$  ion is oxidised to  $\text{N}_2$  by  $\text{HNO}_3$ , which in turn is reduced to  $\text{NO}_2$ . Calculate moles of  $\text{HNO}_3$  required by 1 mole of  $(\text{NH}_4)_2\text{SO}_4$ .



**Plan** From stoichiometric coefficients :

$$\begin{aligned}6\text{ mol HNO}_3(\text{NO}_3^-) &\equiv 2\text{ mol NH}_4^+ \\ &\equiv 1\text{ mol }(\text{NH}_4)_2\text{SO}_4\end{aligned}$$

**Solution** In the product, we find there are two types of nitrogen (as  $\text{N}_2$  and as  $\text{NO}_2$ ). To know which nitrogen is from which reactant, isotopes of nitrogen are used. If N of  $\text{NH}_4^+$  is labelled by its certain isotope, we find that nitrogen certainly appears in  $\text{N}_2$

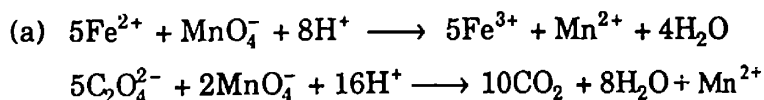


hence, one mole of  $(\text{NH}_4)_2\text{SO}_4$  is oxidised by six moles of  $\text{HNO}_3$ .

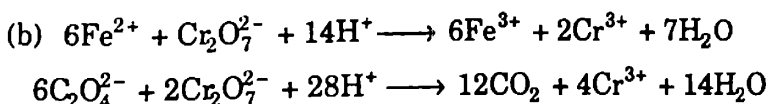
**Problem 5.** Calculate number of moles of (a)  $\text{MnO}_4^-$  and (b)  $\text{Cr}_2\text{O}_7^{2-}$  to oxidise 1 mole of  $\text{FeC}_2\text{O}_4$  (ferrous oxalate) in acidic medium.

**Plan**  $\text{Fe}^{2+}$  and  $\text{C}_2\text{O}_4^{2-}$  (in  $\text{FeC}_2\text{O}_4$ ) both are oxidised by  $\text{MnO}_4^-/\text{H}^+$  as well as by  $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$ . Thus, on comparison of stoichiometric coefficients, number of moles of  $\text{Cr}_2\text{O}_7^{2-}$  and that of  $\text{MnO}_4^-$  required by 1 mole of  $\text{FeC}_2\text{O}_4$  can be calculated.

**Solution**  $\text{Fe}^{2+}$  is oxidised to  $\text{Fe}^{3+}$  and  $\text{C}_2\text{O}_4^{2-}$  is oxidised to  $\text{CO}_2$  both by  $\text{MnO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  in acidic medium.

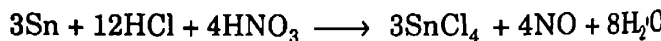


$$\begin{aligned}\text{Thus,} \quad 5\text{FeC}_2\text{O}_4 &\equiv 3\text{MnO}_4^- \\ \therefore 1\text{ mol FeC}_2\text{O}_4 &\equiv 0.6\text{ mol MnO}_4^-\end{aligned}$$



$$\begin{aligned}\text{Thus,} \quad 6\text{FeC}_2\text{O}_4 &\equiv 3\text{Cr}_2\text{O}_7^{2-} \\ \therefore 1\text{ mol FeC}_2\text{O}_4 &\equiv 0.5\text{ mol of Cr}_2\text{O}_7^{2-}\end{aligned}$$

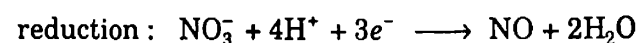
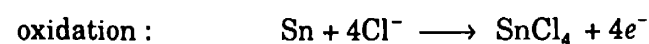
**Problem 6.** The following is a completely balanced equation:



In this reaction, what fraction of the formula weights are the equivalent weights of Sn and  $\text{HNO}_3$  respectively?

$$\begin{aligned}\text{Plan Equivalent weight} &= \frac{\text{formula weight}}{\text{change in oxidation number}} \\ \text{or} &= \frac{\text{formula weight}}{\text{number of electrons exchanged}}\end{aligned}$$

**Solution** The half-reactions are



$$\text{Equivalent weight of Sn} = \frac{\text{formula weight}}{4}$$

Thus, in the oxidation, there are 4 equivalents Sn per mol Sn.

$$\text{Equivalent weight of HNO}_3 = \frac{\text{formula weight}}{3}$$

Thus, in the reduction, there are 3 equivalents  $\text{HNO}_3$  per mol  $\text{HNO}_3$ .

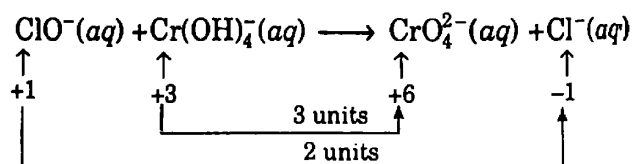
**Problem 7.** Aqueous solution of sodium hypochlorite ( $\text{NaOCl}$ ) is a household bleach and is a strong oxidising agent that reacts with chromite ion  $[\text{Cr}(\text{OH})_4^-]$  in basic solution to yield chromate ( $\text{CrO}_4^{2-}$ ) and chloride ion. Determine

- number of equivalents of each reactant
- number of moles of  $\text{NaOCl}$  required by 1 mole of  $[\text{Cr}(\text{OH})_4^-]$ .

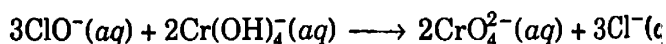
**Plan** (a) Number of equivalents = number moles  $\times$  change in oxidation number

(b) If change in oxidation number of each reactant known, stoichiometric coefficients are also known. Hence number of moles of  $\text{NaOCl}$  can be determined.

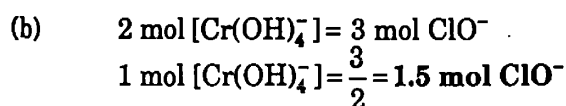
**Solution**



Thus,

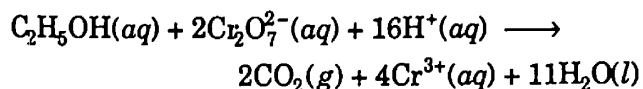


- Equivalents of  $\text{ClO}^-(\text{aq})$  used =  $3 \times 2 = 6$   
Equivalents of  $\text{Cr}(\text{OH})_4^-(\text{aq})$  used =  $2 \times 3 = 6$



**Note :** Remember, in a redox reaction, number of equivalents of each reactant is always same.

**Problem 8.** Alcohol levels in the blood can be determined by a redox titration with dichromate solution in acidic medium according to the balanced equation.



What is the blood alcohol level in mass per cent if 8.76 mL of 0.05 M  $\text{Cr}_2\text{O}_7^{2-}$  solution is required for titration of a 10.00 g sample of blood?

**Plan** Based on stoichiometric coefficients, number of millimol (= molarity  $\times$  mL) of  $\text{Cr}_2\text{O}_7^{2-}$  are to be related to

millimol of alcohol hence, mass per cent of alcohol level in blood can be determined.

**Solution** 2 millimol of  $\text{Cr}_2\text{O}_7^{2-}$  solution

= 1 millimol of  $\text{C}_2\text{H}_5\text{OH}$

8.76  $\times$  0.05 millimol of  $\text{Cr}_2\text{O}_7^{2-}$  solution

$$= \frac{1}{2} \times 8.76 \times 0.05 \text{ millimol of } \text{C}_2\text{H}_5\text{OH}$$

$$= 0.219 \text{ millimol}$$

$$= 0.219 \times 10^{-3} \text{ mol}$$

$$= 0.219 \times 10^{-3} \times 46 \text{ g } \text{C}_2\text{H}_5\text{OH}$$

$$= 0.01 \text{ g } \text{C}_2\text{H}_5\text{OH}$$

Thus, 10 g blood sample has = 0.01 g  $\text{C}_2\text{H}_5\text{OH}$

hence, alcohol level (mass per cent) =  $\frac{0.01}{10} \times 100$

$$= 0.10\%$$



# Master Exercises

## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

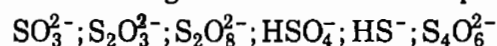
1. When  $\text{Cl}^-$  is converted into  $\text{Cl}_2$ , what is change in oxidation number?
2. What is oxidation number of oxygen in superoxide ion  $\text{O}_2^-$ ?
3. Equivalent weight of  $\text{MnO}_4^-$  is equal to molecular weight, when it changes into new species X. What is X? It is by oxidation or reduction.
4. What is equivalent weight of  $\text{NaHC}_2\text{O}_4$  when  
(a) it behaves as an acid?  
(b) it behaves as a reducing agent?
5. Oxidation number of sulphur in  $\text{H}_2\text{SO}_5$  is +6. Explain by structure.
6. Oxidation number of sulphur in  $\text{H}_2\text{S}_2\text{O}_8$  is +6. Explain by structure.
7. Derive equivalent weight of  
(i)  $\text{H}_3\text{PO}_2$                       (ii)  $\text{H}_3\text{PO}_3$   
(iii)  $\text{H}_3\text{PO}_4$   
at every stage of neutralisation by NaOH.
8. When  $\text{CO}_2$  is passed into aqueous  $\text{K}_2\text{CrO}_4$  solution (yellow), it changes to orange coloured solution. Explain by reaction.
9. When  $\text{SO}_2$  gas is passed into aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  solution (orange), it changes to green coloured solution. Explain by reaction.
10.  $\text{Fe}^{2+}$  is oxidised to  $\text{Fe}^{3+}$  by  $\text{MnO}_4^-$  or  $\text{Cr}_2\text{O}_7^{2-}$  in acidic medium. Explain by reaction with change in colour.

### Analytical Questions

#### Oxidation Number

1. The ion  $\text{A}^{n+}$  is oxidised to  $\text{AO}_3^-$  by  $\text{MnO}_4^-$ , changing to  $\text{Mn}^{2+}$  in acidic solution. Given that  $2.68 \times 10^{-3}$  mol of  $\text{A}^{n+}$  requires  $1.61 \times 10^{-3}$  mol of  $\text{MnO}_4^-$ . What is the value of  $n$ ?

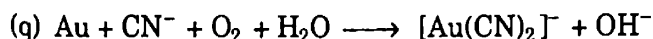
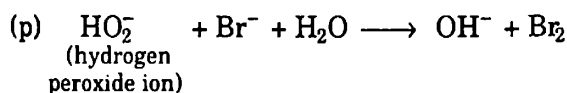
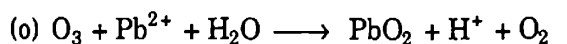
2. Arrange the following sulphur containing anions in order of increasing oxidation state of sulphur:



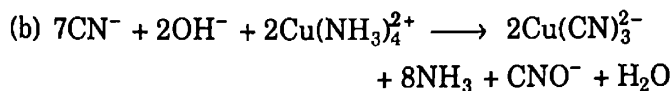
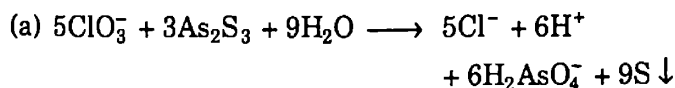
3. Nitrogen forms five different compounds with oxygen. Write appropriate formulae for these compounds if the oxidation state of N in them is +1, +2, +3, +4 and +5.
4. A compound is made of Ba (oxidation number = +2), Xe (oxidation number = 8) and oxygen. Xe and O are present in the atomic ratio of 1:6, what is the compound?
5.  $\text{KMnO}_4$  oxidises  $\text{X}^{n+}$  ion into  $\text{XO}_3^-$ , itself changing to  $\text{Mn}^{2+}$  in acid solution.  $2.68 \times 10^{-3}$  mol of  $\text{X}^{n+}$  requires  $1.61 \times 10^{-3}$  mol of  $\text{MnO}_4^-$ . What is atomic weight of X if the weight of 1 g equivalent of  $\text{XCl}_n$  is 56?

### Redox Reactions

6. Balance the following redox reactions. Also underline disproportionation reactions:
  - (a)  $\text{MnO}_4^- + \text{I}^- + \text{H}^+ \longrightarrow \text{Mn}^{2+} + \text{I}_2 + \text{H}_2\text{O}$
  - (b)  $\text{Cl}_2 + \text{I}^- + \text{H}_2\text{O} \longrightarrow \text{IO}_3^- + \text{Cl}^- + \text{H}^+$
  - (c)  $\text{BrO}_3^- + \text{N}_2\text{H}_4 \longrightarrow \text{Br}^- + \text{N}_2 + \text{H}_2\text{O}$
  - (d)  $\text{VO}_4^{3-} + \text{Fe}^{2+} + \text{H}^+ \longrightarrow \text{VO}^{2+} + \text{Fe}^{3+} + \text{H}_2\text{O}$
  - (e)  $\text{UO}_2^{2+} + \text{Cr}_2\text{O}_7^{2-} + \text{H}^+ \longrightarrow \text{UO}_2^{2+} + \text{Cr}^{3+} + \text{H}_2\text{O}$
  - (f)  $\text{Pb}(\text{NO}_3)_2 \longrightarrow \text{PbO} + \text{NO}_2 + \text{O}_2$
  - (g)  $\text{IO}_3^- + \text{HSO}_4^- + \text{H}^+ \longrightarrow \text{I}_2 + \text{SO}_4^{2-} + \text{H}_2\text{O}$
  - (h)  $\text{S}_2\text{O}_4^{2-} + \text{H}_2\text{O} \longrightarrow \text{S}_2\text{O}_3^{2-} + \text{HSO}_3^-$
  - (i)  $\text{Cl}_2 + \text{OH}^- \longrightarrow \text{ClO}^- + \text{Cl}^- + \text{H}_2\text{O}$
  - (j)  $\text{C}_6\text{H}_5\text{CHO} + \text{OH}^- \longrightarrow \text{C}_6\text{H}_5\text{COO}^- + \text{C}_6\text{H}_5\text{CH}_2\text{O}^-$
  - (k)  $\text{S}_2\text{O}_3^{2-} + \text{H}^+ \longrightarrow \text{H}_2\text{O} + \text{SO}_2 + \text{S}$
  - (l)  $\text{Cl}^- + \text{NO}_3^- + \text{H}^+ \longrightarrow \text{NO}_2 + \text{Cl}_2 + \text{H}_2\text{O}$
  - (m)  $\text{ClO}^- + \text{H}_2\text{O} \longrightarrow \text{ClO}_2^- + \text{Cl}_2 + \text{OH}^-$
  - (n)  $\text{Cl}_2 + \text{S}^{2-} \longrightarrow \text{S} + \text{Cl}^-$

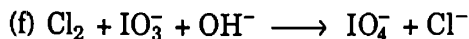
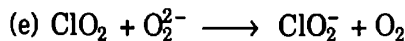
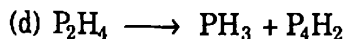
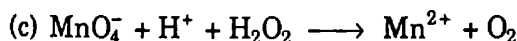
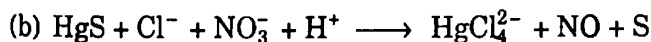
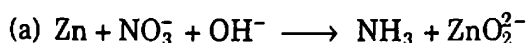


7. Identify the oxidising agent and the reducing agent in the following redox reactions:



8.  $\text{H}_2\text{O}_2$  can be used as oxidising agent or reducing agent depending on the medium. Explain, why this behaviour is possible? Give one example of each.

9. Balance the following redox reactions:



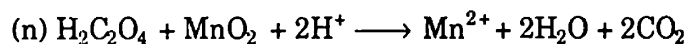
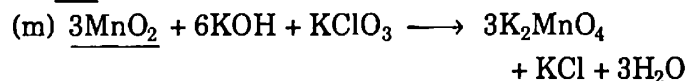
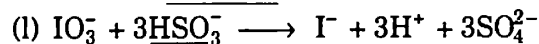
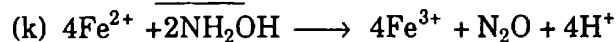
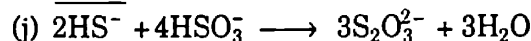
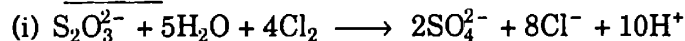
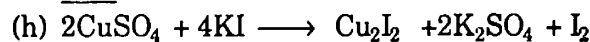
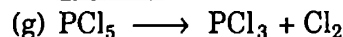
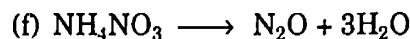
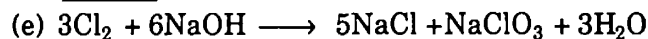
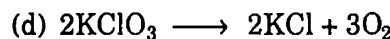
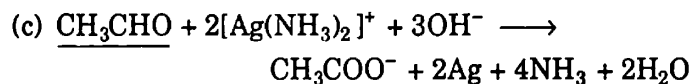
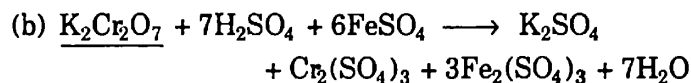
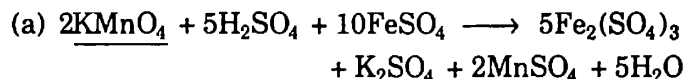
10. Calculate the number of moles of  $\text{MnO}_4^-$  that will be needed to react with one mole of  $\text{SO}_3^{2-}$  (sulphite ion) in acidic solution.

11.  $\text{H}_2\text{O}_2$  acts both as an oxidising agent and as a reducing agent in alkaline solution towards first row transition metal ions. Illustrate both these properties of  $\text{H}_2\text{O}_2$  using chemical equations.

12. Give an example of oxidation of one halide by another halogen. Explain the feasibility of the reaction.

## Equivalent Weight

13. Determine the equivalent weight of the underlined by taking its molecular weight as  $M$ :

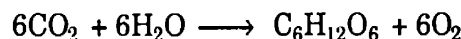


14. Photosynthesis of a carbohydrate in plants is given by chemical equation



Calculate:

- equivalents of  $\text{O}_2$  formed per mol of  $\text{CO}_2$  consumed.
- equivalents of  $\text{C}_6\text{H}_{12}\text{O}_6$  per mol of  $\text{H}_2\text{O}$  used.
- equivalents of  $\text{CO}_2$  used per mol of  $\text{H}_2\text{O}$  used.
- If you have net result as:



It is correct or incorrect? Explain.

## Exercise 2

### (Stage 2 : High Skill Problem Solving)

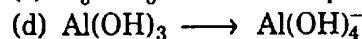
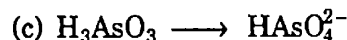
#### Only One Option Correct

1. A sulphur-containing species that can't be a reducing agent is

- $\text{SO}_2$
- $\text{SO}_3^{2-}$
- $\text{H}_2\text{SO}_4$
- $\text{S}^{2-}$

2. Which of the following changes requires a reducing agent?

- $\text{CrO}_4^{2-} \longrightarrow \text{Cr}_2\text{O}_7^{2-}$
- $\text{BrO}_3^- \longrightarrow \text{BrO}^-$



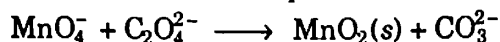
3. In balancing the half-reaction



the number of electrons that must be added is

- 0
- 1 on the right
- 1 on the left
- 2 on the right

4. For the reaction between  $\text{MnO}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$  in basic solution, the unbalanced equation is



In a balanced equation, the number of  $\text{OH}^-$  ions is

- (a) 0 (b) 4 on the right  
(c) 4 on the left (d) 2 on the left
5. Which of the following is disproportionation reaction?
- (a)  $\text{CaCO}_3 + 2\text{H}^+ \longrightarrow \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2$   
(b)  $2\text{CrO}_4^{2-} + 2\text{H}^+ \longrightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$   
(c)  $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \longrightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$   
(d)  $\text{Cu}_2\text{O} + 2\text{H}^+ \longrightarrow \text{Cu} + \text{Cu}^{2+} + \text{H}_2\text{O}$
6. When  $\text{MnO}_4^-$  and  $\text{I}^-$  react in a strongly basic solution, the products will most likely be
- (a) Mn and  $\text{I}_2$  (b)  $\text{MnO}_4^{2-}$ ,  $\text{IO}_3^-$   
(c)  $\text{MnO}_2$ ,  $\text{O}_2$ ,  $\text{IO}^-$  (d)  $\text{Mn}^{2+}$ ,  $\text{I}_2$
7. Of the following acids, the one that is strongest is
- (a)  $\text{HBrO}_4$  (b)  $\text{HOCl}$   
(c)  $\text{HNO}_2$  (d)  $\text{H}_3\text{PO}_3$
8. When  $\text{PbS}(\text{s})$  is treated with warm dilute  $\text{HNO}_3$ , the products most likely will be
- (a)  $\text{Pb}^{2+}$ , S,  $\text{NO}_2$  (b)  $\text{Pb}^{2+}$ , S, NO  
(c)  $\text{PbO}$ , S, NO (d)  $\text{PbO}_2$ ,  $\text{SO}_4^{2-}$ ,  $\text{N}_2$
9. In an experiment 20 g of vanadium (V) oxide (molar mass = 182) was reduced by excess of zinc dust in acidic solution to vanadium (II) ions. The required number of moles of iodine to reoxidise vanadium (II) to  $\text{VO}^{2+}$  is
- (a) 0.22 (b) 0.11  
(c) 0.30 (d) 0.23
10. For a titration of  $100 \text{ cm}^3$  of  $0.1 \text{ M Sn}^{2+}$  to  $\text{Sn}^{4+}$ ,  $50 \text{ cm}^3$  of  $0.40 \text{ M Ce}^{4+}$  solution was required. The oxidation state of cerium in the reduction product is
- (a) +1 (b) +2  
(c) +3 (d) 0
11. In the following reaction (unbalanced), equivalent weight of  $\text{As}_2\text{S}_3$  is related to molecular weight  $M$  by
- $$\text{As}_2\text{S}_3 + \text{H}^+ + \text{NO}_3^- \longrightarrow \text{NO} + \text{H}_2\text{O} + \text{AsO}_4^{3-} + \text{SO}_4^{2-}$$
- (a)  $\frac{M}{2}$  (b)  $\frac{M}{4}$   
(c)  $\frac{M}{28}$  (d)  $\frac{M}{24}$
12. 1 mole of  $\text{FeC}_2\text{O}_4$  is oxidised by  $x$  mole of  $\text{Cr}_2\text{O}_7^{2-}$  in acidic medium,  $x$  is
- (a) 3 (b) 1.5  
(c) 0.5 (d) 1.0
13. 1 mole of  $\text{MnO}_4^-$  will oxidise  $x$  mole of ferric oxalate in acidic medium,  $x$  is
- (a)  $\frac{5}{6}$  (b)  $\frac{6}{5}$   
(c) 5 (d) 6
14. In the reaction, 4 moles of electrons are transferred and 1 mole of  $\text{HNO}_3$ . The possible product obtained due to reduction
- (a) 0.4 mol of  $\text{N}_2$   
(b) 0.5 mol of  $\text{N}_2\text{O}$   
(c) 1 mol of  $\text{NO}_2$   
(d) 1 mol of  $\text{NH}_3$
15. 1 mole of  $\text{N}_2\text{H}_4$  loses 10 mol of electrons to form a new compound Y. Assuming that all the nitrogen appear in the new compound, what is the oxidation state of nitrogen in Y? (no change in the oxidation state of H)
- (a) -1 (b) -3  
(c) +3 (d) +5
16. Oxidation number of P in  $\text{Ba}(\text{H}_2\text{PO}_2)_2$  is
- (a) +3 (b) +2  
(c) +1 (d) -1
17. Which combination appears odd w.r.t. oxidation number per atom of the underlined?
- (a)  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{S}_2$ ,  $\text{K}_2\text{S}_2\text{O}_7$   
(b)  $\text{CrO}_5$ ,  $\text{CrO}_4^{2-}$ ,  $\text{SO}_4^{2-}$   
(c) Both (a) and (b)  
(d) None of the above
18. In  $[\text{Cr}(\text{O}_2)(\text{NH}_3)_4(\text{H}_2\text{O})]\text{Cl}_2$  oxidation number of Cr is +3, then  $\text{O}_2$  will be in the form
- (a) dioxo (b) peroxo  
(c) superoxo (d) oxo
19. Strongest conjugate base is
- (a)  $\text{ClO}^-$  (b)  $\text{ClO}_2^-$   
(c)  $\text{ClO}_3^-$  (d)  $\text{ClO}_4^-$
20. Which is not a disproportionation reaction?
- (a)  $2 \text{C}_6\text{H}_5\text{CHO} \xrightarrow{\text{Al}(\text{OEt})_3} \text{C}_6\text{H}_5\text{COOCH}_2\text{C}_6\text{H}_5$
- (b)  $\begin{array}{c} \text{CHO} \\ | \\ \text{COOH} \end{array} + \text{OH}^- \longrightarrow \begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{COO}^- \end{array} + \begin{array}{c} \text{COO}^- \\ | \\ \text{COO}^- \end{array}$
- (c)  $\text{NaH} + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{H}_2$   
(d) All of the above
21. Oxidation number of Cr in the following compound are  $x$ ,  $y$ ,  $z$  and  $w$ .
- $\text{K}[\text{Cr}(\text{O}_2)(\text{OH})]$ ,  $\text{K}_3[\text{Cr}(\text{O}_2)_4]$ ,  $(\text{NH}_3)_3[\text{Cr}(\text{O}_2)_2]$ ,  $\text{CrO}_2\text{Cl}_2$
- These values are
- (a) 6, 13, 5, 6 (b) 4, 4, 4, 6  
(c) 4, 5, 4, 6 (d) 4, 5, 6, 6

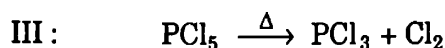
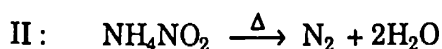
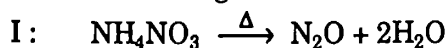
22. If a small amount of  $\text{KMnO}_4$  is added to conc.  $\text{H}_2\text{SO}_4$ , a green coloured solution with oxidation number of Mn as +7 is formed. Probable compound is  
 (a)  $\text{MnO}_3\text{HSO}_4$  (b)  $\text{K}_2\text{MnO}_4$   
 (c)  $\text{MnO}_2\text{HSO}_4$  (d)  $\text{MnO}_2$

23. Equivalent weight of  $\text{Mn}^{3+}$  in the following reaction is (Mn = 55)



- (a) 27.5 (b) 55  
 (c) 110 (d) 165
24. Which of the following is the example of a disproportionation reaction?  
 (a)  $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$   
 (b)  $2\text{HCuCl}_2 \longrightarrow \text{Cu} + \text{Cu}^{2+} + 4\text{Cl}^- + 2\text{H}^+$   
 (c)  $\text{PCl}_5 \longrightarrow \text{PCl}_3 + \text{Cl}_2$   
 (d)  $2\text{H}_2\text{S} + \text{SO}_2 \longrightarrow 3\text{S} + 2\text{H}_2\text{O}$

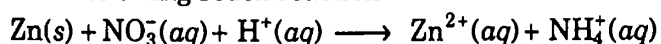
25. Out of the following redox reactions



disproportionation is not shown in

- (a) I, II (b) II, III  
 (c) I, III (d) I, II and III
26. Bleaching powder ( $\text{CaOCl}_2$ ) has two types of chlorine atoms with oxidation number of +1 and -1. It can be represented as:  
 (a)  $\text{Ca}^{2+}(\text{ClO}_2^-)\text{Cl}^-$   
 (b)  $\text{Ca}^{2+}(\text{ClO}_3^-)\text{Cl}^-$   
 (c)  $\text{Ca}^{2+}(\text{ClO}^+)\text{Cl}^-$   
 (d)  $\text{Ca}^{2+}(\text{ClO}^-)\text{Cl}^-$

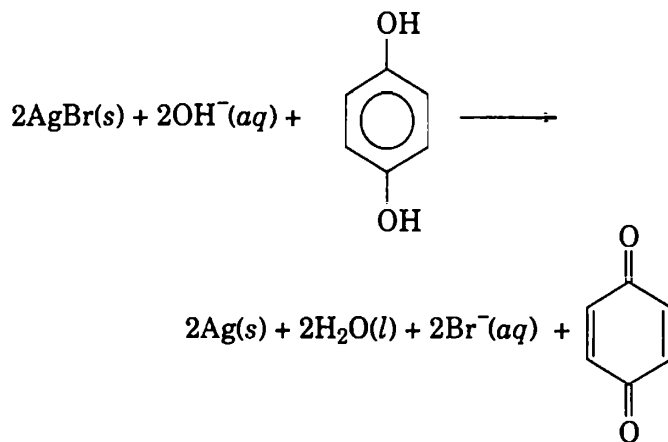
27. In the following redox reaction



$\text{Zn(s)}$  and  $\text{NO}_3^-(\text{aq})$  respectively are:

- (a) oxidant, reductant  
 (b) reductant, oxidant  
 (c) both oxidant  
 (d) both reductant
28. Out of the following select species with different oxidation states of the underlined atoms  
 I:  $\text{CaO}\underline{\text{Cl}}_2$ ; II:  $\text{H}_2\underline{\text{S}}_2\text{O}_8$ ; III:  $\text{Na}_2\underline{\text{S}}_4\text{O}_6$   
 IV:  $\text{Cr}\underline{\text{O}}_5$ ; V:  $\text{N}_2\underline{\text{H}}_4\text{O}_3$   
 (a) All except I  
 (b) All except II  
 (c) All except III  
 (d) All except IV

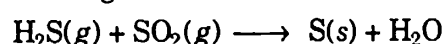
29. Photographic paper is developed with alkaline hydroquinone

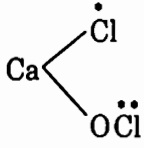
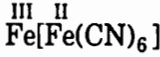


Select correct statement.

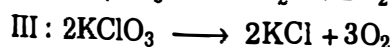
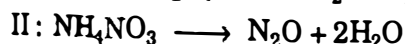
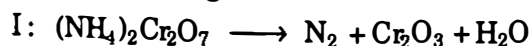
- (a) Hydroquinone is the oxidant  
 (b)  $\text{Ag}^+$  is the oxidant  
 (c)  $\text{Br}^-$  is the oxidant  
 (d)  $\text{Ag}^+$  is the reductant
30. In the following redox reaction  
 $\text{Cu(OH)}_2(\text{s}) + \text{N}_2\text{H}_4(\text{aq}) \longrightarrow \text{Cu(s)} + \text{N}_2(\text{g})$   
 number of moles of  $\text{Cu(OH)}_2$  reduced by one mole of  $\text{N}_2\text{H}_4$  is  
 (a) 1 (b) 2  
 (c) 3 (d) 4
31. In the following half-reaction in basic medium  
 $\text{Bi}^{3+}(\text{aq}) \longrightarrow \text{BiO}_3^-(\text{aq})$   
 one mole of  $\text{Bi}^{3+}$  is equivalent to  
 (a) 1 (b) 2  
 (c) 3 (d) 4
32. The complex  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  is formed in the ring-test for nitrate when freshly prepared  $\text{FeSO}_4$  solution is added to aqueous solution of  $\text{NO}_3^-$  followed by addition of conc.  $\text{H}_2\text{SO}_4$ . This complex is formed by charge transfer in which  
 (a)  $\text{Fe}^{2+}$  changes to  $\text{Fe}^{3+}$  and  $\text{NO}^+$  changes to  $\text{NO}$   
 (b)  $\text{Fe}^{2+}$  changes to  $\text{Fe}^{3+}$  and  $\text{NO}$  changes to  $\text{NO}^+$   
 (c)  $\text{Fe}^{2+}$  changes to  $\text{Fe}^+$  and  $\text{NO}$  changes to  $\text{NO}^-$   
 (d) no charge transfer takes place
33. When KCN is added to  $\text{CuSO}_4$  solution there is formation of the stable water soluble complex. This complex is  
 (a)  $\text{K}_4[\text{Cu}(\text{CN})_6]$  (b)  $\text{K}_3[\text{Cu}(\text{CN})_4]$   
 (c)  $\text{K}_2[\text{Cu}(\text{CN})_4]$  (d)  $\text{K}[\text{Cu}(\text{CN})_3]$
34. In cyanide method, silver metal is obtained as  
 $2\text{K}[\text{Ag}(\text{CN})_2] + \text{Zn} \longrightarrow \text{K}_2[\text{Zn}(\text{CN})_4] + 2\text{Ag}$   
 In this  
 (a) Ag has been oxidised and Zn has been reduced  
 (b)  $\text{Ag}^+$  has been reduced and Zn has been oxidised  
 (c) both the metals have been oxidised  
 (d) both the metals have been reduced.

35. In the following unbalanced redox reaction



- total number of equivalent of  $\text{SO}_2$  is  
 (a) 4 (b) 3  
 (c) 2 (d) 1
36. In the above reaction of question (35), one equivalent of  $\text{H}_2\text{S}(g)$  will reduce  
 (a) 1 mol of  $\text{SO}_2$  (b) 0.5 mol of  $\text{SO}_2$   
 (c) 0.25 mol of  $\text{SO}_2$  (d) 2 mol of  $\text{SO}_2$
37. Which has maximum number of equivalent per mol of the oxidant?  
 (a)  $\text{Zn}(s) + \text{VO}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{V}^{3+}(aq)$   
 (b)  $\text{Ag}(s) + \text{NO}_3^-(aq) \longrightarrow \text{Ag}^+(aq) + \text{NO}_2(g)$   
 (c)  $\text{Mg}(s) + \text{VO}_4^{3-}(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{V}^{2+}(aq)$   
 (d)  $\text{I}^-(aq) + \text{IO}_3^-(aq) \longrightarrow \text{I}_3^-(aq)$
38. Which has maximum oxidation number of the underlined atom in the following?  
 (a)  $\text{MnO}_4^{2-}$  (b)  $\text{CrO}_5$   
 (c)  $\text{CrO}_2\text{Cl}_2$  (d) Equal
39. Which has least number of equivalent per mol of the reactant?  
 (a)  $\text{MnO}_4^-$  changes to  $\text{MnO}_2$   
 (b)  $\text{MnO}_4^-$  changes to  $\text{Mn}^{2+}$   
 (c)  $\text{MnO}_4^-$  changes to  $\text{MnO}_4^{2-}$   
 (d)  $\text{MnO}_4^-$  changes to  $\text{Mn}_2\text{O}_3$
40. Oxidation number of Cr is +5 in  
 (a)  $\text{K}_3\text{CrO}_8$  (b)  $(\text{NH}_3)_3\text{CrO}_4$   
 (c)  $\text{K}_2\text{CrO}_4$  (d)  $[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$
41. Sulphur atoms are of two environments in  $\text{S}_4\text{O}_6^{2-}$ , difference in oxidation states of two types of sulphur is  
 (a) 5 (b) 6  
 (c) 7 (d) 10
42. When  $\text{Br}_2$  is passed into hot aqueous solution of  $\text{Na}_2\text{CO}_3$ ,  
 (a)  $\text{Br}^-$  is formed by reduction  
 (b)  $\text{BrO}_3^-$  is formed by oxidation  
 (c)  $\text{CO}_2$  is evolved  
 (d) all of the above are correct
43. Consider following unbalanced reactions  
 I :  $\text{Zn} + \text{dil. H}_2\text{SO}_4 \longrightarrow \text{ZnSO}_4 + \text{H}_2$   
 II :  $\text{Zn} + \text{conc. H}_2\text{SO}_4 \longrightarrow \text{ZnSO}_4 + \text{SO}_2 + \text{H}_2\text{O}$   
 III :  $\text{Zn} + \text{HNO}_3 \longrightarrow \text{Zn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + \text{H}_2\text{O}$   
 Oxidation number of hydrogen changes in  
 (a) I, II, III (b) I, II  
 (c) II, III (d) I
44.  $\text{NH}_3$  is oxidised to  $\text{NO}$  by  $\text{O}_2$  (air) in basic medium. Number of equivalent of  $\text{NH}_3$  oxidised by 1 mole of  $\text{O}_2$  is  
 (a) 4 (b) 5  
 (c) 6 (d) 7
45. In the following redox reactions,  $\text{NH}_3$  appears either in reactant or product. In which case equivalent weight of  $\text{NH}_3$  is maximum?  
 (a)  $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$   
 (b)  $4\text{NH}_3 + 5\text{O}_2 \longrightarrow 4\text{NO} + 6\text{H}_2\text{O}$   
 (c)  $2\text{NH}_3 + 2\text{Na} \longrightarrow 4\text{NaNH}_2 + \text{H}_2$   
 (d) Equal in the above all cases
46. In the following unbalanced redox reaction,  
 $\text{Cu}_3\text{P} + \text{Cr}_2\text{O}_7^{2-} \longrightarrow \text{Cu}^{2+} + \text{H}_3\text{PO}_4 + \text{Cr}^{3+}$   
 Equivalent weight of  $\text{H}_3\text{PO}_4$  is  
 (a)  $\frac{M}{3}$  (b)  $\frac{M}{6}$   
 (c)  $\frac{M}{7}$  (d)  $\frac{M}{8}$
47. In the following reaction  
 $\text{Zn} + 2\text{OH}^- + 2\text{H}_2\text{O} \longrightarrow \text{Zn}(\text{OH})_4^{2-} + \text{H}_2$   
 Species which has been reduced is  
 (a) Zn (b)  $\text{OH}^-$   
 (c)  $\text{H}_2\text{O}$  (d) none of these
48.  $\text{H}_2\text{S}_2\text{O}_8$  and  $\text{H}_2\text{SO}_5$  both have +6 oxidation state of sulphur. It is due to  
 (a) presence of peroxy group  
 (b) presence of superoxo group  
 (c) presence of neutral  $\text{O}_2$   
 (d) presence of ozone
49.  $\text{H}_2\text{O}_2$  oxidises  $\text{MnO}_2$  to  $\text{MnO}_4^-$  in basic medium.  $\text{H}_2\text{O}_2$  and  $\text{MnO}_2$  react in the molar ratio of  
 (a) 1 : 1 (b) 2 : 1  
 (c) 2 : 3 (d) 3 : 2
50. Equivalent weight of  $\text{H}_3\text{PO}_2$  in a reaction is found to be half of its molecular weight. It can be due to its  
 (a) reaction of its two  $\text{H}^+$  ions  
 (b) oxidation to  $\text{H}_3\text{PO}_3$   
 (c) both (a) and (b)  
 (d) None of the above
51. Oxidation number of Cl atoms in  $\text{CaOCl}_2$  are  
  
 (a) zero on each  
 (b) -1 on Cl and +1 on Cl  
 (c) +1 on Cl and -1 on Cl  
 (d) +1 on each
52. Prussian blue has two types of iron with oxidation number as shown  
  
 What is the net charge on Prussian blue?  
 (a) -1 (b) +1  
 (c) 0 (d) -2

53. Consider following redox reactions



Select intramolecular redox reactions

(a) I, II

(b) II, III

(c) I, III

(d) I, II, III

54. 0.05 mole of  $\text{Ca}(\text{OH})_2$  can neutralise  $\text{H}_2\text{SO}_4$ . This  $\text{H}_2\text{SO}_4$  can be neutralised by

(a) 0.05 mol of NaOH

(b) 0.10 mol of NaOH

(c) 0.05 mol of  $\text{POH}(\text{OH})_2$

(d) None of the above is correct

55.  $\text{NaHC}_2\text{O}_4$  is neutralised by NaOH and can also be oxidised by  $\text{KMnO}_4$  (in acidic medium). Equivalent weight is related to molecular weight ( $M$ ) of  $\text{NaH}_2\text{C}_2\text{O}_4$  in these reactions as

(a)  $M, M$

(b)  $\frac{M}{2}, \frac{M}{2}$

(c)  $\frac{M}{2}, M$

(d)  $M, \frac{M}{2}$

56. If  $\text{OX}_1 + ae^- \rightleftharpoons \text{Red}_1, E_1^\circ$

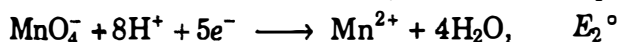
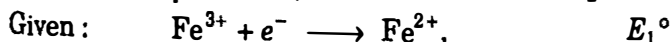


Then potential at the equivalence point is

$$(a) E = \frac{aE_1^\circ + bE_2^\circ}{(a+b)} \quad (b) E = \frac{aE_1^\circ - bE_2^\circ}{(a+b)}$$

$$(c) E = \frac{bE_2^\circ - aE_1^\circ}{(a+b)} \quad (d) E = \frac{aE_1^\circ - bE_2^\circ}{(a-b)}$$

57. In the following redox reaction,



Potential at the equivalence point is

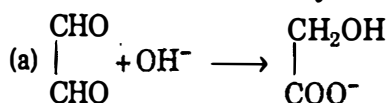
$$(a) E = (E_1^\circ + E_2^\circ) - 0.08 \text{ pH}$$

$$(b) E = \frac{E_1^\circ + 5E_2^\circ}{6} - 0.08 \text{ pH}$$

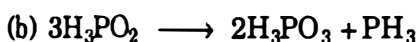
$$(c) E = (E_1^\circ - E_2^\circ) - 0.08 \text{ pH}$$

$$(d) E = \frac{E_1^\circ - 5E_2^\circ}{6} + 0.08 \text{ pH}$$

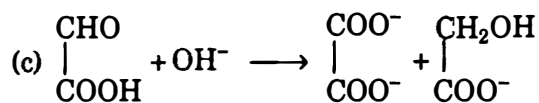
58. Which reaction is suitably matched?



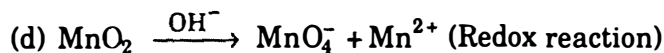
(crossed Cannizzaro reaction)



(disproportionation reaction)



(Intramolecular Cannizzaro reaction)



59. If  $\text{CO}_2$  is passed into waste water containing  $\text{CrO}_4^{2-}$  (yellow) then

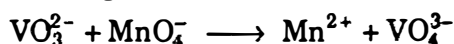
(a) solution turn green due to formation of  $\text{Cr}^{3+}$

(b) solution turns blue due to formation of  $\text{CrO}_5$

(c) solution turns orange due to formation of  $\text{Cr}_2\text{O}_7^{2-}$

(d) no effect takes place

60. In the following reaction



1 mole of  $\text{VO}_3^{2-}$  is oxidised by  $\text{MnO}_4^-$

(a) 0.2 mol

(b) 0.4 mol

(c) 0.8 mol

(d) 1.0 mol

## One or More Than One Options Correct

1. One mole of ferric oxalate is titrated with acidified potassium permanganate solution. In this

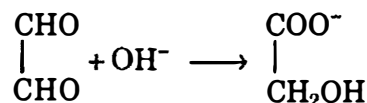
(a) 3 mol of potassium permanganate are required

(b) 1.2 mol of potassium permanganate are required.

(c) oxalate ion is oxidised to carbon dioxide.

(d) ferric ion is oxidised to ferrate (VI) ion

2. Consider following reaction :



(a) It is a disproportionation reaction

(b) It is intramolecular redox reaction

(c)  $\text{OH}^-$  is a reducing as well as oxidising agent

(d)  $\begin{array}{c} \text{CHO} \\ | \\ \text{CHO} \end{array}$  is a reducing as well as oxidising agent

3. Out of  $\text{FeO}_4^{2-}$ ,  $\text{FeCl}_3$ ,  $\text{FeCl}_2$  and Fe,

(a) best reducing agent is Fe

(b) best oxidising agent is  $\text{FeO}_4^{2-}$

(c) best oxidising agent is  $\text{FeCl}_3$

(d) best reducing agent is  $\text{FeO}_4^{2-}$

4. 0.1 mol of  $\text{NaHC}_2\text{O}_4$  is

(a) neutralised by 0.1 mol of NaOH

(b) neutralised by 0.05 mol of  $\text{Ca}(\text{OH})_2$

(c) oxidised by 0.04 mol of  $\text{KMnO}_4$  in acidic medium

(d) oxidised by 0.02 mol of  $\text{K}_2\text{MnO}_4$  in basic medium

## 5. Select correct statements.

Equivalent weight of  $\text{KMnO}_4$  (molar mass =  $M$ ) is

- (a)  $\frac{M}{5}$  in acidic medium  
 (b)  $\frac{M}{3}$  in neutral basic medium  
 (c)  $M$  in strongly alkaline medium  
 (d)  $\frac{M}{2}$  in acidic, basic and neutral media

## 6. Intramolecular redox reactions are

- (a)  $\text{PCl}_5 \longrightarrow \text{PCl}_3 + \text{Cl}_2$   
 (b)  $2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$   
 (c)  $\begin{array}{c} \text{CHO} \\ | \\ \text{CHO} \end{array} + \text{OH}^- \longrightarrow \begin{array}{c} \text{COO}^- \\ | \\ \text{CH}_2\text{OH} \end{array}$   
 (d)  $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$

7. Out of  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{S}_2\text{O}_8$ ,  $\text{H}_2\text{SO}_5$ ,  $\text{H}_2\text{S}_2\text{O}_3$  and  $\text{H}_2\text{S}_2\text{O}_7$ 

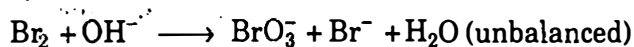
(I) (II) (III) (IV) (V)

- (a) oxidation number of sulphur is +6 in all except IV  
 (b) peroxy linkage is in I, II and III  
 (c) peroxy linkage is in II and III  
 (d) oxidation number of sulphur is -2 in I and V

## 8. Select correct statement(s).

- (a) Equivalent weight of  $\text{Ca}(\text{HC}_2\text{O}_4)_2$  is  $\frac{M}{2}$  when it is a reducing agent  
 (b) Equivalent weight of  $\text{Ca}(\text{HC}_2\text{O}_4)_2$  is  $M$  when it behaves as an acid  
 (c)  $\text{Ca}(\text{HC}_2\text{O}_4)_2$  can be estimated by  $\text{MnO}_4^-/\text{H}^+$   
 (d)  $\text{Ca}(\text{HC}_2\text{O}_4)_2$  can be estimated by an acid

## 9. Consider following reaction



Select correct statement.

- (a) Equivalent weight of  $\text{Br}_2$  when it is reduced to  $\text{Br}^-$  is 80  
 (b) Equivalent weight of  $\text{Br}_2$  when it is oxidised to  $\text{BrO}_3^-$  is 96  
 (c) Net equivalent weight of  $\text{Br}_2$  is 96  
 (d) It is a disproportionation reaction
10. Following is/are disproportionation reaction(s)  
 (a)  $2\text{CCl}_3\text{CHO} + \text{NaOH} \longrightarrow \text{CCl}_3\text{COONa} + \text{CCl}_3\text{CH}_2\text{OH}$   
 (b)  $\text{NH}_4\text{NO}_3 \longrightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$   
 (c)  $2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$   
 (d)  $5\text{Cl}_2 + 6\text{OH}^- \longrightarrow \text{ClO}_3^- + 5\text{Cl}^- + 3\text{H}_2\text{O}$

## Passage Comprehension Questions

## Passage 1

Consider following Redox Predominance Diagram for iron in different oxidation state

| Oxidation state | Half-reaction                                                                                           | $E^\circ/\text{V}$ |
|-----------------|---------------------------------------------------------------------------------------------------------|--------------------|
| +6              | $\text{FeO}_4^{2-} + 8\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{Fe}^{3+} + 4\text{H}_2\text{O}$ | +2.20 V            |
| +3              | $\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$                                            | +0.77 V            |
| +2              | $\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}$                                             | -0.44 V            |

Answers the following questions.

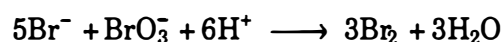
1. Select best oxidising and reducing agent  
 (a)  $\text{Fe}$ ,  $\text{Fe}^{2+}$  (b)  $\text{FeO}_4^{2-}$ ,  $\text{Fe}^{3+}$   
 (c)  $\text{FeO}_4^{2-}$ ,  $\text{Fe}^{2+}$  (d)  $\text{FeO}_4^{2-}$ ,  $\text{Fe}$
2. Most thermodynamically stable species is  
 (a)  $\text{FeO}_4^{2-}$  (b)  $\text{Fe}^{3+}$   
 (c)  $\text{Fe}^{2+}$  (d)  $\text{Fe}$
3. Least thermodynamically species is  
 (a)  $\text{FeO}_4^{2-}$  (b)  $\text{Fe}^{3+}$   
 (c)  $\text{Fe}^{2+}$  (d)  $\text{Fe}$

## Passage 2

Every disproportionation reaction is a redox reaction but every redox reaction may not be disproportionation. Disproportionation reaction may be intramolecular if same species is oxidised and reduced.

Based on the above statement answer the following questions.

1. A:  $2\text{C}_6\text{H}_5\text{CHO} + \text{KOH} \longrightarrow \text{C}_6\text{H}_5\text{COOK} + \text{C}_6\text{H}_5\text{CH}_2\text{OH}$   
 B:  $3\text{Cl}_2 + 6\text{KOH} \longrightarrow 5\text{KCl} + \text{KClO}_3 + 3\text{H}_2\text{O}$   
 Select correct statement.  
 (a) Both are redox reactions  
 (b) Both are disproportionation reaction  
 (c) A is a disproportionation and B is a redox reaction  
 (d) A is a redox reaction, B is a disproportionation reaction
2. Following reaction is used to produce  $\text{Br}_2$



In this reaction,

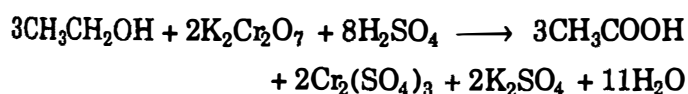
- (a)  $\text{Br}^-$  disproportionates to  $\text{Br}_2$   
 (b)  $\text{BrO}_3^-$  disproportionates to  $\text{Br}_2$   
 (c)  $\text{Br}^-$  has been oxidised and  $\text{BrO}_3^-$  has been reduced  
 (d)  $\text{Br}^-$  has been reduced and  $\text{BrO}_3^-$  has been oxidised.

### Passage 3

Following passage is for the drunken drivers on roads which are becoming fatal by their wrong driving.

Every year in our country about 25,000 people are killed and 500,000 more are injured as a result of drunk driving. In spite of efforts to educate the public about the dangers of driving while intoxicated and stiffer penalties for drunk driving offenses, law enforcement agencies still have to devote a great deal of work to remove drunk drivers from roads.

The police often use a device called a breath analyser to test drivers suspected to being drunk. The chemical basis of this device is a redox reaction. A sample of the driver's breath is drawn into the breath analyser, where it is treated with an acidic solution of potassium dichromate.



The driver's blood alcohol level can be determined readily by measuring the degree of this colour change (read from a calibrated meter on the instrument). The current legal limit of blood alcohol content is 0.1 per cent by mass. Anything higher constitutes intoxication.

Read the passage and answer the questions given below:

1. Above test is based on

- smell of ethanol and ethanoic acid
- change of colour yellow to blue
- change of colour orange to green
- change of colour orange to colourless

2. Equivalent mass of  $\text{K}_2\text{Cr}_2\text{O}_7$  is

- |                                   |                                   |
|-----------------------------------|-----------------------------------|
| (a) $\frac{\text{molar mass}}{6}$ | (b) $\frac{\text{molar mass}}{3}$ |
| (c) $\frac{\text{molar mass}}{2}$ | (d) $\frac{\text{molar mass}}{1}$ |

3. Equivalent mass of  $\text{CH}_3\text{CH}_2\text{OH}$  is

- $\frac{\text{molar mass}}{1}$
- $\frac{\text{molar mass}}{2}$
- $\frac{\text{molar mass}}{3}$
- $\frac{\text{molar mass}}{4}$

4. The alcohol content in a 10.0 g sample of blood from a driver required 4.23 mL of 0.07654 M  $\text{K}_2\text{Cr}_2\text{O}_7$  for titration. Should the police prosecute the individual for drunken driving.

- yes
- no
- nothing can be predicted
- None of the above

### Assertion & Reason

Codes :

- Both A and R are true and R is the correct explanation of A
- Both A and R are true but R is not the correct explanation of A
- A is true but R is false
- A is false but R is true

1. **Assertion (A) :**  $\text{NH}_4\text{NO}_3$  undergoes a redox reaction to  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$ .

**Reason (R) :** It is a disproportionation reaction.

2. **Assertion (A) :** Oxidation number of sulphur in  $\text{H}_2\text{SO}_6$  is +6.

**Reason (R) :** It has one peroxy linkage.

3. **Assertion (A) :** Oxidation number of chromium in  $\text{CrO}_5$  is +6.

**Reason (R) :** Oxidation number of each oxygen atom is -1.5.

4. **Assertion (A) :**  $\text{Br}_2$  is oxidised to  $\text{BrO}_3^-$  in basic medium.

**Reason (R) :** When  $\text{Br}_2$  is passed into hot  $\text{NaOH}$ , it disproportionates to  $\text{Br}^-$  and  $\text{BrO}_3^-$ .

5. **Assertion (A) :** 1 mole of  $\text{FeC}_2\text{O}_4$  is oxidised by 0.6 mole of  $\text{MnO}_4^-$  in acidic medium.

**Reason (R) :**  $\text{MnO}_4^-$  oxidises both  $\text{Fe}^{2+}$  as well as  $\text{C}_2\text{O}_4^{2-}$ .

### True & False

- Lewis structures should have adjacent formal charges of zero or of opposite sign.
- Oxidation number of sulphur in  $\text{H}_2\text{SO}_6$  is +6.



- Oxidation number of sulphur in  $\text{H}_2\text{S}_2\text{O}_8$  is +7.
- Following reaction is disproportionation reaction,  

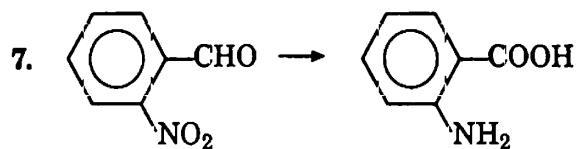
$$\text{NH}_4^+ + \text{NO}_3^- \longrightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$$
- $\text{SO}_3^{2-}$  is named as sulphate (IV).
- $\text{HCHO}$  disproportionates in presence of  $\text{OH}^-$ .
- Oxidation number of iron in brown complex (obtained in ring-test of  $\text{NO}_3^-$ ) is +1.  

$$[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$$
- Equivalent weight of  $\text{MnO}_4^-$  when it changes to  $\text{MnO}_2$  in concentrated basic medium is one-fifth of molar mass.
- Oxidation number of chromium in  $\text{CrO}_2^{2+}$  is +6.
- Oxidation number of each chlorine in  $\text{CaOCl}_2$  is -1.

### Fill in the Blanks

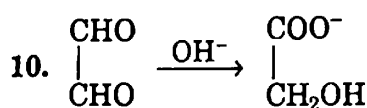
- Oxidation number of Mn in  $\text{MnO}_2$ ,  $\text{MnO}_4^{2-}$  and  $\text{MnO}_4^-$  are....., ..... and ..... respectively.
- Oxidation number of Mn in  $\text{MnO}_3\text{Cl}$  is .....
- $\text{Br}_2$  disproportionates to ..... and ..... in cold  $\text{Na}_2\text{CO}_3$  solution.
- Equivalent weight of  $\text{Cl}_2$  in the following reaction is .....  

$$\text{Cl}_2 \longrightarrow \text{ClO}_3^- + \text{Cl}^-$$
- Oxidation number of Fe in  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]$  is +1 due to charge transfer .....
- $\text{CrO}_5$  has oxidation number of Cr as +6 hence, it has .....



This reaction is ..... redox-reaction.

- 1 mole of  $\text{Cr}_2\text{O}_7^{2-}$  oxidises ..... moles of  $\text{FeC}_2\text{O}_4$  in acidic medium.
- In copper extraction, final stage reaction is .....



is a type of ..... reaction.

### Matrix-Match Type Questions

#### I. Only One Correct

- Match the different compounds of Mn (in List I) with oxidation number (in List II).

| List I                         | List II |
|--------------------------------|---------|
| A. $\text{MnO}_3\text{HSO}_4$  | 1. +4   |
| B. $\text{K}_2\text{MnO}_4$    | 2. +7   |
| C. $\text{MnO}_2$              | 3. +6   |
| D. $\text{Mn}_2\text{O}_3$     | 4. +2   |
| E. $\text{Mn}(\text{HCO}_3)_2$ | 5. +3   |

- Match the half-reactions (in List I) with change in oxidation number (in List II).

| List I                                                   | List II |
|----------------------------------------------------------|---------|
| A. $\text{Cl}^- \longrightarrow \text{ClO}_4^-$          | 1. 2    |
| B. $\text{Cr}^{3+} \longrightarrow \text{CrO}_5$         | 2. 8    |
| C. $\text{H}_2\text{O}_2 \longrightarrow \text{O}_2$     | 3. 0    |
| D. $\text{CrO}_2^{2+} \longrightarrow \text{CrO}_4^{2-}$ | 4. 3    |

#### II. One or More Correct

- Match the compounds in Column I with the matter in Column II.

| Column I                                            | Column II                                           |
|-----------------------------------------------------|-----------------------------------------------------|
| A. $\text{H}_2\text{S}_2\text{O}_8$                 | 1. Peroxy linkage                                   |
| B. $\text{CrO}_5$                                   | 2. Oxidation number of the underlined atom 6        |
| C. $\text{H}_2\text{SO}_5$                          | 3. $\text{H}_2\text{O}_2$ is the hydrolysis product |
| D. $\text{K}_2\text{CrO}_4$                         | 4. Caro's acid                                      |
| E. $(\text{NH}_3)_3\text{Cr}^{\text{IV}}\text{O}_4$ | 5. Marshall's acid                                  |

- Match the compounds/Ions having underlined atoms of different oxidation states in Column I with values in Column II.

| Column I                                             | Column II |
|------------------------------------------------------|-----------|
| A. $\text{CaOCl}_2$                                  | 1. 6      |
| B. $\text{Na}_2\text{S}_2\text{O}_3$                 | 2. 3      |
| C. $\text{N}_2\text{H}_4\text{O}_2$                  | 3. 2      |
| D. $[\text{Fe}_2(\text{CN})_6]^-$<br>(Prussian blue) | 4. -1     |
| E. $\text{CrO}_5$                                    | 5. 1      |
|                                                      | 6. -2     |
|                                                      | 7. -3     |

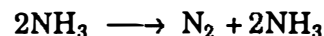
### Integer Answer Types

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the ORS have to be darkened. For example, if the correct answers to question number *X*, *Y*, *Z* and *W* (say) are 6, 0, 9 and 2, respectively, then

| X                       | Y                       | Z                       | W                       |
|-------------------------|-------------------------|-------------------------|-------------------------|
| <input type="radio"/> 0 | <input type="radio"/> 0 | <input type="radio"/> 0 | <input type="radio"/> 0 |
| <input type="radio"/> 1 | <input type="radio"/> 1 | <input type="radio"/> 1 | <input type="radio"/> 1 |
| <input type="radio"/> 2 | <input type="radio"/> 2 | <input type="radio"/> 2 | <input type="radio"/> 2 |
| <input type="radio"/> 3 | <input type="radio"/> 3 | <input type="radio"/> 3 | <input type="radio"/> 3 |
| <input type="radio"/> 4 | <input type="radio"/> 4 | <input type="radio"/> 4 | <input type="radio"/> 4 |
| <input type="radio"/> 5 | <input type="radio"/> 5 | <input type="radio"/> 5 | <input type="radio"/> 5 |
| <input type="radio"/> 6 | <input type="radio"/> 6 | <input type="radio"/> 6 | <input type="radio"/> 6 |
| <input type="radio"/> 7 | <input type="radio"/> 7 | <input type="radio"/> 7 | <input type="radio"/> 7 |
| <input type="radio"/> 8 | <input type="radio"/> 8 | <input type="radio"/> 8 | <input type="radio"/> 8 |
| <input type="radio"/> 9 | <input type="radio"/> 9 | <input type="radio"/> 9 | <input type="radio"/> 9 |

1.  $\text{C}_2\text{O}_7^{2-}$  changes to  $\text{Cr}^{3+}$  in acidic medium. Thus, molecular weight of  $\text{C}_2\text{O}_7^{2-} = x \times$  equivalent weight. What is the value of  $x$ ?

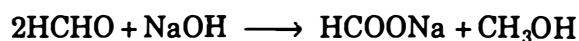
2. In the following reaction



equivalent weight of  $\text{NH}_3$  is  $= \frac{\text{molecular weight}}{y}$

What is value of  $y$ ?

3. In a Cannizzaro reaction of  $\text{HCHO}$  with  $\text{NaOH}$



Molecular weight of  $\text{HCHO} = z \times$  equivalent weight.

What is value of  $z$ ?

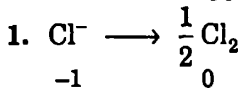
4. Oxidation number of  $\text{Cr}$  in  $(\text{NH}_3)_3\text{Cr}(\text{O}_2)_2$  is .....
5. Number of peroxy linkage in  $\text{K}_3\text{Cr}(\text{O}_2)_x$  having oxidation number of  $\text{Cr}$  as +5 is .....
6. Difference in oxidation states of two types of sulphur in  $\text{S}_4\text{O}_6^{2-}$  is .....
7. Based on redox predominance diagram, out of  $\text{FeO}_4^{2-}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}$ , best oxidising agent is the species with oxidation number of iron as .....
8. Maximum oxidation state of chlorine is .....

# Answers & Solutions

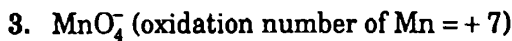
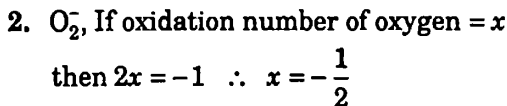
## Master Exercises

### Exercise 1

### Short Answer Type Questions



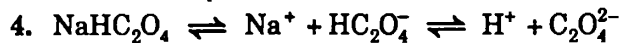
**Change in oxidation number = 1 unit**



It is maximum value of oxidation number. In the product formed, oxidation number should be less than +7.

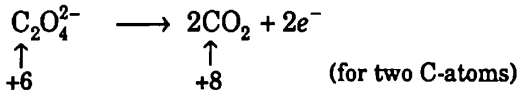
Since, equivalent weight = molecular weight, hence oxidation number of Mn = +6 in new species formed by reduction.

This is  $\text{MnO}_4^{2-}$

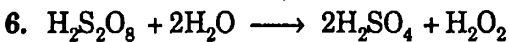
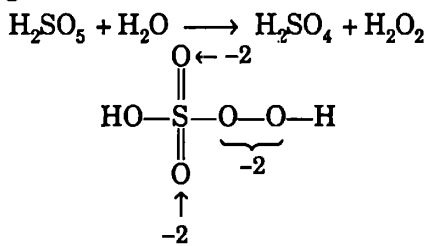
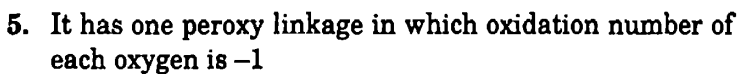


(a) It has one ionisable  $\text{H}^+$  thus equivalent weight = molecular weight

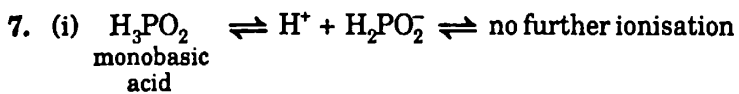
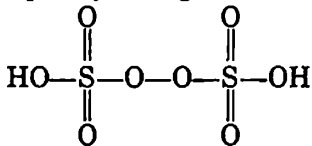
(b)  $\text{C}_2\text{O}_4^{2-}$  is a reducing agent, itself oxidised to  $\text{CO}_2$ .



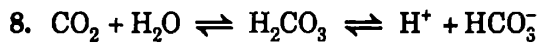
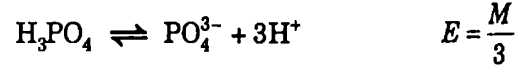
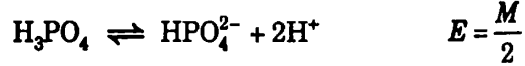
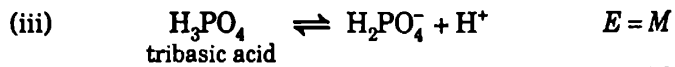
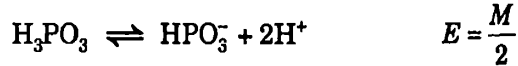
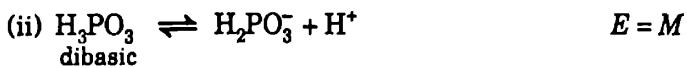
**Change in oxidation number = 2 units**

$$\text{Thus, equivalent weight} = \frac{\text{molecular weight}}{2}$$


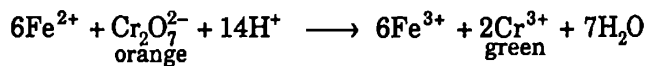
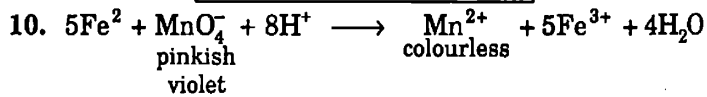
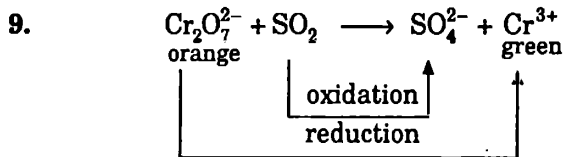
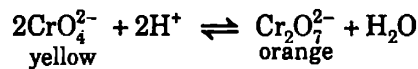
**It has also one peroxy linkage**



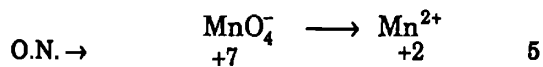
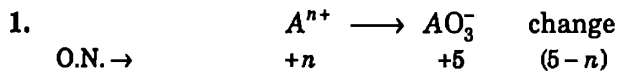
Thus, equivalent weight =  $M$



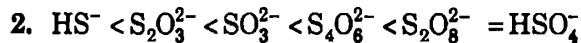
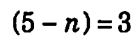
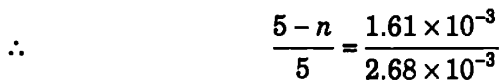
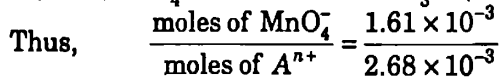
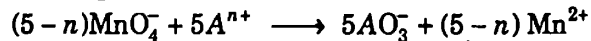
**CO<sub>2</sub> makes the solution acidic, which converts CrO<sub>4</sub><sup>2-</sup> into Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>**



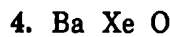
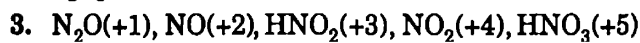
## Analytical Questions



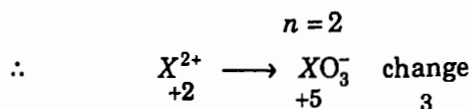
### Balancing (O.N.)



Oxidation state is the oxidation number per atom  
 $\text{S}_2\text{O}_8^{2-}$  has one peroxy linkage.



5. As in 11.



$$\therefore \text{Equivalent mass of } XCl_2 = \frac{M}{3} = 56$$

$$\therefore M = 56 \times 3 = 168$$

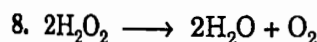
$$XCl_2 = M + 35.5 \times 2 = 168$$

$$\therefore M = 97$$

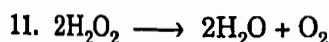
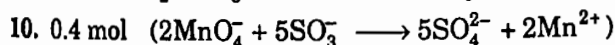
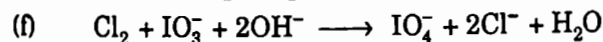
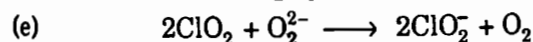
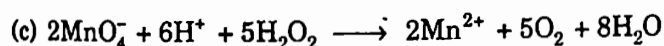
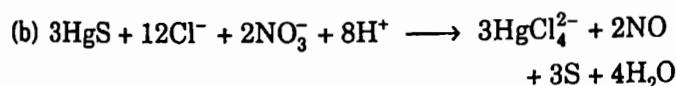
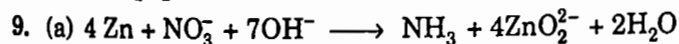
6. Refer Text (h), (l), (j), (k), (m) are disproportionation reaction.

7. **Oxidising agent** (a)  $ClO_3^-$  (b)  $Cu(NH_3)_4^{2+}$

**Reducing agent** (a)  $Ag_2S_3$  (b)  $CN^-$

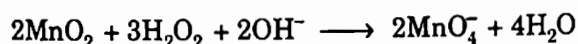


Since,  $H_2O_2$  disproportionates to  $H_2O$  and  $O_2$ .

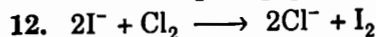
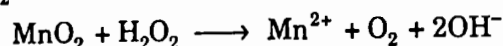


Since,  $H_2O_2$  disproportionates to  $H_2O$  (by reduction) and  $O_2$  (by oxidation) hence acts both as an oxidising agent and as a reducing agent. Examples are

**$H_2O_2$  as oxidising agent**

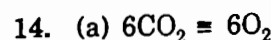
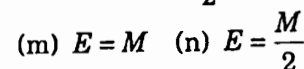
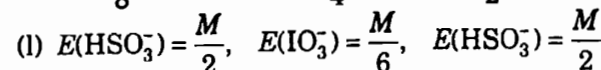
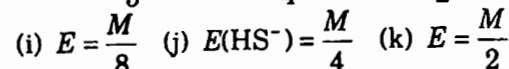
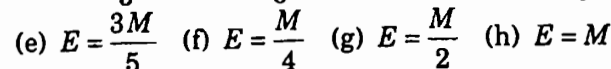
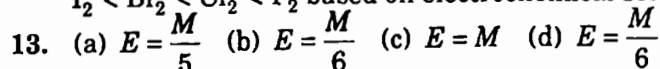


**$H_2O_2$  as reducing agent**

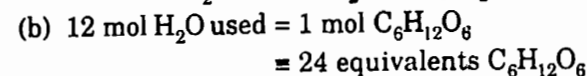


oxidising power is in order:

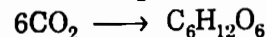
$I_2 < Br_2 < Cl_2 < F_2$  based on electrochemical series.



$$1 \text{ mol } CO_2 \equiv 1 \text{ mol } O_2 \equiv 32 \text{ g } O_2 \equiv 4 \text{ equivalents}$$



$$1 \text{ mol } H_2O \text{ used} \equiv 2 \text{ equivalents } C_6H_{12}O_6$$



$$O.N. = 24 \quad = 0$$

$$\text{change} = 24 \text{ units}$$

$$\text{Equivalent weight of } CO_2 = \frac{6 \text{ mol}}{24} = \frac{\text{mol. wt.}}{4}$$

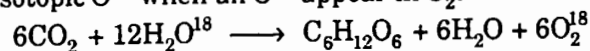
$$\therefore 1 \text{ mol } CO_2 = 4 \text{ equivalents } CO_2$$

$$\text{Equivalent weight of } C_6H_{12}O_6 = \frac{\text{mol. wt.}}{24}$$

$$\therefore 1 \text{ mol } C_6H_{12}O_6 = 24 \text{ equivalents of } C_6H_{12}O_6$$

(c) 2 equivalents of  $CO_2$

(d) No,  $O_2$  (product) is from  $H_2O$  (reactant), hence  $12H_2O$  is taken as reactant. It is confirmed by taking isotopic  $O^{18}$  when all  $O^{18}$  appear in  $O_2$ .



## Exercise 2

### Only One Option Correct

1. If the species is a reducing agent, it means it can be oxidised easily thus it should have an O.N. less than maximum values of O.N.

|             | O.N. |                                                        |
|-------------|------|--------------------------------------------------------|
| $SO_2$      | 4    | } $SO_2, SO_3^{2-}$ and $S^{2-}$ can be reducing agent |
| $SO_3^{2-}$ | 4    |                                                        |
| $SO_4^{2-}$ | 6    |                                                        |
| $S^{2-}$    | -2   |                                                        |
| but         |      | $SO_4^{2-}$ can't be.                                  |

Thus, (c)

2. (a,d) no change

(b) reduction, (c) oxidation

Thus, (b)



$$\begin{array}{ccc} \text{O.N. of nitrogen} & 4 + x = -1 & 4 + x - 2 = -1 \\ & x = -5 & x = -3 \end{array}$$

$CN^-$  is thus oxidised. Thus, two electrons are lost. Thus, (d)

4. (c) 5. (d) 6. (b)

7. Strongest acid is that which has maximum value of O.N. of the central atom



Thus, (a)

8. (b)

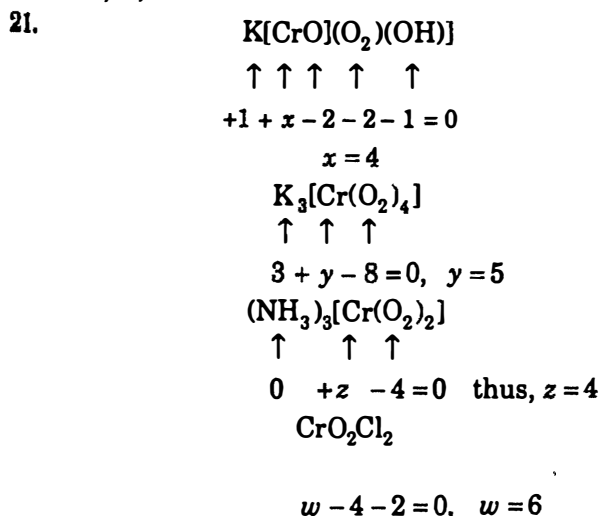


H<sup>+</sup> changes to H<sub>2</sub> — reduction

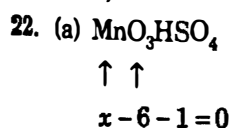
Thus, different H are involved.

Thus, it is a redox but not disproportionation.

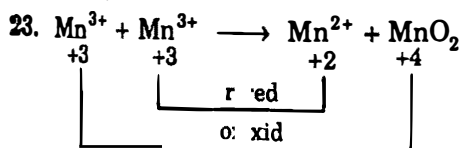
Thus, (c)



Thus, (c)



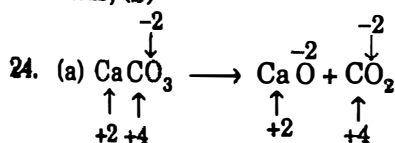
Thus, (a)



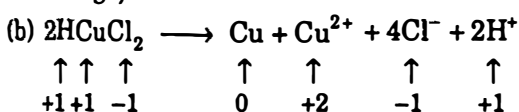
Mn<sup>3+</sup> disproportionates to Mn<sup>2+</sup> and MnO<sub>2</sub>

Thus, equivalent mass of Mn<sup>3+</sup> =  $\frac{2 \text{ units of Mn}^{3+}}{2}$   
 $= \frac{M}{2} = 55$

Thus, (b)

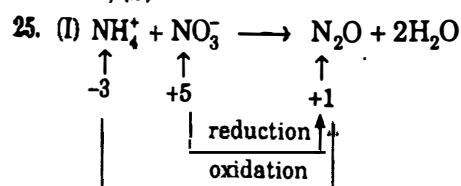


No change,

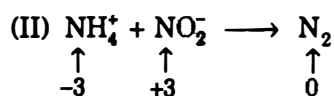


Thus, Cu<sup>+</sup> disproportionates to Cu and Cu<sup>2+</sup>.

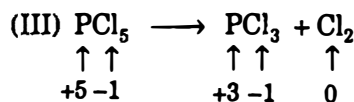
Thus, (b)



It is a redox but not disproportionation. Since, different N-species are involved.



Same as (I)

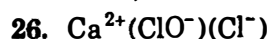


P<sup>+5</sup> is reduced to P<sup>3+</sup>

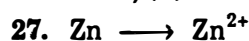
Cl<sup>-</sup> is oxidised to Cl<sub>2</sub>

Thus, different species are involved. Thus, it is also not a disproportionation reaction.

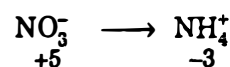
Thus, (d)



Thus, (d)

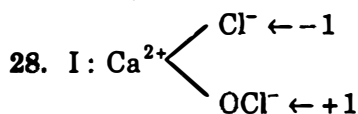


Zn is oxidised hence, it is a reducing agent (reductant)



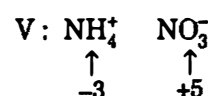
NO<sub>3</sub><sup>-</sup> is reduced hence, it is oxidising agent (oxidant)

Thus, (b)



II: +6 both and S

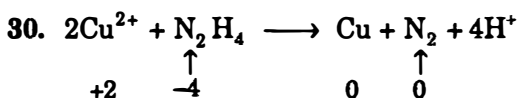
III: 0 and 5 IV -2, 1



Thus, (b)

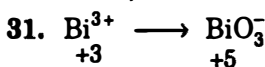
29. Ag<sup>+</sup> is reduced hence, it is oxidant. Hydroquinone is oxidised hence, it is reductant.

Thus, (b)



∴ Thus 1 mol N<sub>2</sub>H<sub>4</sub> ≡ 2 mol Cu<sup>2+</sup>

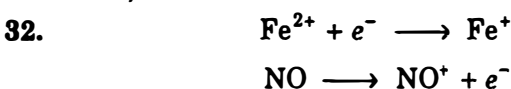
Thus, (b)



Change in oxidation number = 2 units

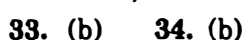
Thus, number of equivalents in one mole Bi<sup>3+</sup> = 2

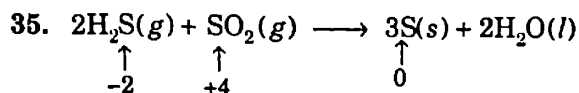
Thus, (b)



Based on magnetic properties of the complex, it is found that iron has three unpaired electrons thus it is as Fe<sup>3+</sup> formed by reduction of Fe<sup>2+</sup> by NO which is oxidised to NO<sup>+</sup>.

Thus, (c)

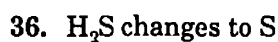




Change in oxidation number = 4 units

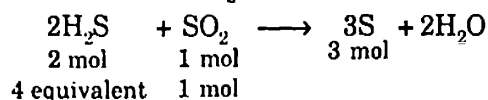
Thus, number of equivalent of  $\text{SO}_2 = 4$

Thus, (a)



Thus, change in oxidation number = 2 units

Thus, one equivalent  $\text{H}_2\text{S} = 2$

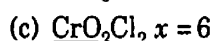
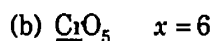


1 equivalent of  $\text{H}_2\text{S}$  will reduce 0.25 mol of  $\text{SO}_2$

Thus, (c)

| 37. | Reaction                                                                                                                                                                  | Change in O.N. | Number of equivalent |
|-----|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|----------------------|
| (a) | $\underset{\substack{\uparrow \uparrow \\ x-2 = +2 \\ x = +4}}{\text{VO}^{2+}}(\text{aq}) \longrightarrow \underset{\substack{\uparrow \\ +3}}{\text{V}^{3+}}(\text{aq})$ | 1 unit         | 1                    |
| (b) | $\underset{\substack{\uparrow \\ +5}}{\text{NO}_3^-}(\text{aq}) \longrightarrow \underset{\substack{\uparrow \\ +4}}{\text{NO}_2}(\text{g})$                              | 1 unit         | 1                    |
| (c) | $\underset{\substack{\uparrow \\ +5}}{\text{VO}_4^{3-}}(\text{aq}) \longrightarrow \underset{\substack{\uparrow \\ +2}}{\text{V}^{2+}}(\text{aq})$                        | 3 unit         | 3                    |
| (d) | $\underset{\substack{\uparrow \\ +5}}{\text{IO}_3}(\text{aq}) \longrightarrow \underset{\substack{\uparrow \\ -1 \\ -3}}{\text{I}_3^-}(\text{aq})$                        | $\frac{16}{3}$ | $\frac{16}{3}$       |

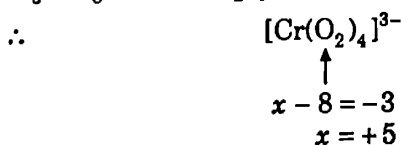
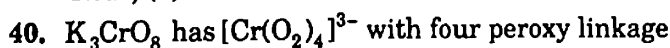
Thus, (d)



Thus, (d)

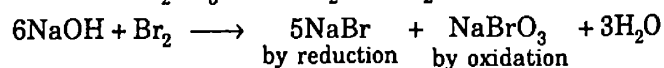
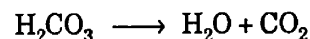
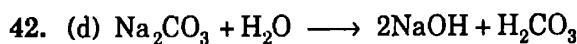
| 39.                                                                                                                           | Change in O.N. | Equivalent per mol of $\text{MnO}_4^-$ |
|-------------------------------------------------------------------------------------------------------------------------------|----------------|----------------------------------------|
| (a) $\underset{\substack{\uparrow \\ +7}}{\text{MnO}_4^-} \longrightarrow \underset{\substack{\uparrow \\ +4}}{\text{MnO}_2}$ | 3              | 3                                      |
| (b) $\longrightarrow \underset{\substack{\uparrow \\ +2}}{\text{Mn}^{2+}}$                                                    | 5              | 5                                      |
| (c) $\longrightarrow \underset{\substack{\uparrow \\ +6}}{\text{MnO}_4^{2-}}$                                                 | 1              | 1                                      |
| (d) $\longrightarrow \frac{1}{2} \underset{\substack{\uparrow \\ +3}}{\text{Mn}_2\text{O}_3}$                                 | 4              | 4                                      |

Thus, (c)

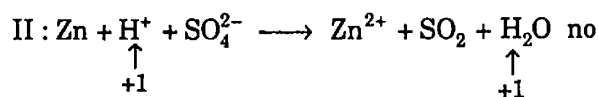
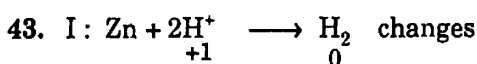


Thus, (a)

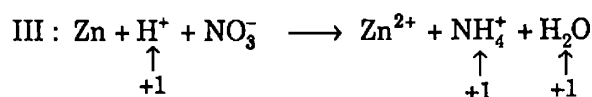
41. (a)



Thus, (d)

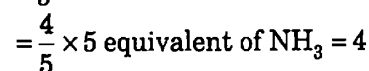
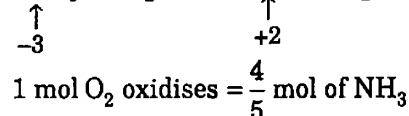
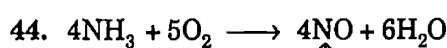


change

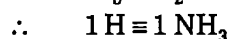
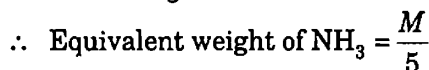
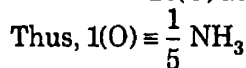
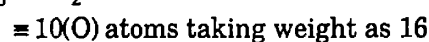
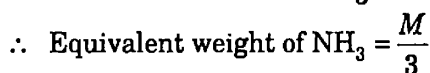


Thus, in (I) only

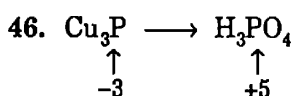
Thus, (d)



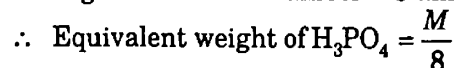
Thus, (a)



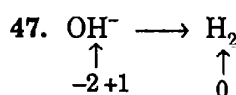
Thus, (c)



Change in oxidation number = 8 units of phosphorus



Thus, (d)



Thus,  $\text{OH}^-$  is reduced to  $\text{H}_2$

Thus, (b)

48.  $\text{H}_2\text{S}_2\text{O}_8$    
peroxy linkage

$\text{H}_2\text{SO}_5$  

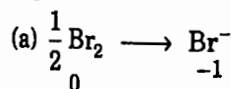
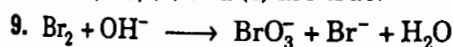




$\text{Ca}(\text{HC}_2\text{O}_4)_2$  cannot be estimated by acid

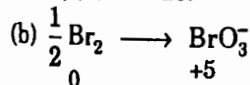
Thus, (d) is not true

Thus, (a), (b) and (c) are true.



Equivalent weight =  $\frac{M}{2} = 80$

Thus, (a) is true.



Equivalent weight =  $\frac{M}{10} = \frac{160}{10} = 16$

Thus, (b) is not true

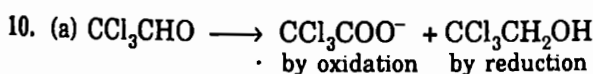
(c) Net equivalent weight = Equivalent (in oxidation part + in reduction part)  
 $= 16 + 80 = 96$

Thus, (c) is true

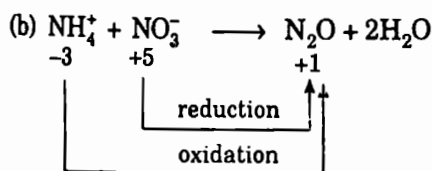
(d)  $\text{Br}_2$  disproportionates to  $\text{Br}^-$  (reduction) and  $\text{BrO}_3^-$  (oxidation)

Thus, (d) is also true.

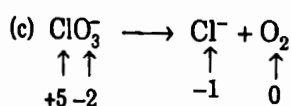
Thus, (a), (c) and (d) true.



Thus, (a) is true

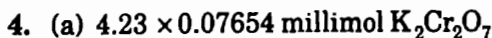


Different ions are involved, hence (b) is not true



(d) Different atoms are involved, hence (c) is not true (d) is true (refer question 9(d)).

Thus, (a) and (d) are true



$\equiv 4.23 \times 0.07654 \times 6$  milliequivalent of  $\text{K}_2\text{Cr}_2\text{O}_7$

$\equiv 4.23 \times 0.07654 \times 6$  milliequivalent of  $\text{CH}_3\text{CH}_2\text{OH}$

$\equiv \frac{4.23 \times 0.07654 \times 6 \times 23}{1000} \text{ g CH}_3\text{CH}_2\text{OH}$

$\equiv 0.045 \text{ g in } 10 \text{ g sample}$

Thus, % of alcohol content =  $\frac{0.045}{10} \times 100$

$= 0.45 > 0.10$

Thus, (a)

## Assertion & Reason

1. (c)    2. (a)    3. (c)    4. (d)    5. (a)

## True & False

1. T    2. T    3. F    4. F    5. T    6. T    7. T  
 8. F    9. T    10. F

## Fill in the Blanks

1. +4, +6, +7    2. +7    3.  $\text{Br}^-$ ,  $\text{BrO}^-$     4. 42.6  
 5. from NO to  $\text{Fe}^{2+}$     6. two peroxy linkages  
 7. intramolecular    8. 2    9. disproportionation  
 10. intramolecular disproportionation.

## Matrix-Match Type Questions

### I. Only One Correct

1. (A) — (2); (B) — (3); (C) — (1);  
 (D) — (5); (E) — (4)  
 2. (A) — (2); (B) — (4); (C) — (1); (D) — (3);

### II. One or More Correct

1. (A) — (1,2,3,5); (B) — (1,2); (C) — (1,2,3);  
 (D) — (2); (E) — (1)  
 2. (A) — (4,5); (B) — (1,6); (C) — (2,7);  
 (D) — (2,3); (E) — (4,6)

## Integer Answer Types

| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|-------------|---|---|---|---|---|---|---|---|
| Answers →   | 6 | 3 | 1 | 4 | 4 | 5 | 6 | 7 |
| ①           | ① | ① | ① | ① | ① | ① | ① | ① |
| ②           | ② | ② | ② | ② | ② | ② | ② | ② |
| ③           | ③ | ③ | ③ | ③ | ③ | ③ | ③ | ③ |
| ④           | ④ | ④ | ④ | ④ | ④ | ④ | ④ | ④ |
| ⑤           | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ |
| ⑥           | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ |
| ⑦           | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ |
| ⑧           | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ |
| ⑨           | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ |

## Passage Comprehension Questions

### Passage 1

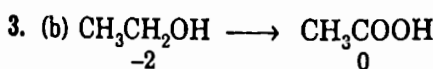
1. (d)    2. (a)    3. (d)

### Passage 2

1. (b)    2. (c)

### Passage 3

1. (c)    2. (a)



Change in O.N. = 2 units

Thus,  $E = \frac{M}{2}$



**"If the radiance of a thousand suns  
were to be burst into the sky, that  
would be like the splendour of the  
mighty one — yet when the sinister  
and gigantic clouds rose up .....**

**I am become death, the shatters of  
world ....."**

**A passage from Bhagvad Gita was  
quoted by Robert Jungk in his  
book while describing the first  
testing of Atom Bomb in Japan.**

5

# Radioactivity

## Quick Points

- Elements in the Periodic Table, have been placed in the increasing order of atomic number.
- In the element  ${}^A_pX$ ,  
 $A$  = atomic mass = proton + neutron =  $p + n$   
 $p$  = proton = atomic number = electrons in neutral atom
- $E = mc^2$  by Einstein equation, where  $m$  is the mass and  $c$  the velocity of light.
- By first-order kinetics,

$$\text{rate, } -\frac{dN}{dt} = \lambda N$$

where  $\lambda$  = disintegration constant

(also called rate constant) in  $\text{time}^{-1}$  unit

$$\lambda = \frac{2.303}{t} \log_{10} \frac{N_0}{N}$$

where  $N_0$  is the number of atoms disintegrating at start and  
 $N$  is the number of atoms disintegrating at time  $t$ .

- When 50% disintegration has taken place

$$N = \frac{N_0}{2}, t = t_{50} \text{ called half-life period}$$

$$t_{50} = \frac{2.303 \log 2}{\lambda} = \frac{0.693}{\lambda}$$

Thus,  $t_{50}$  is independent of initial number of atoms.

## Learning Framework of the Chapter

- Radioactivity
- Units of Radioactivity
- Theory of Radioactive Disintegration
- Nuclear Stability
- Nuclear Reactions
- Nuclear Fission
- Nuclear Fusion
- Artificial Radioactivity
- Binding Energy and Packing Fraction
- Applications of Radioactive Isotopes
- Radiations and Matter : Detection and Biological Effects

- Also,  $N = N_0 \left(\frac{1}{2}\right)^y$   
where  $y = \frac{\text{total time}}{t_{50}}$

## Radioactivity

Radioactivity was discovered by **Henri Becquerel** in 1896, while investigating any possible relation between fluorescence and X-rays. A crystal of potassium uranyl sulphate was used as a source of fluorescence material. On exposure to sunlight, it emitted radiations which could penetrate paper, glass and aluminium sheets and ionise gases. These types of radiations were also observed in darkness. Nature and origin of these radiations were investigated by Becquerel, Rutherford, Pierre Curie and Marie Curie. Uranium changed to thorium during the emission of these radiations.

Radioactivity is the phenomenon of spontaneous disintegration of certain nuclei to form new elements with the emission of “active radiation”, they are called active as they affect photographic plates and interact with electric and magnetic fields. Active radiations are summarised in Table 5.1.

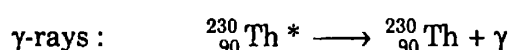
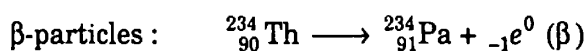
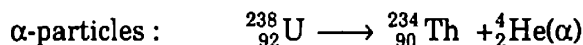


Table 5.1 Types of Radioactive Decay

| Types of decay                  | Radiation         | Equivalent process                         | Nuclear change |             | Usual nuclear condition |
|---------------------------------|-------------------|--------------------------------------------|----------------|-------------|-------------------------|
|                                 |                   |                                            | Atomic number  | Mass number |                         |
| Alpha emission ( $\alpha$ )     | ${}_2^4\text{He}$ | —                                          | — 2            | — 4         | $Z > 83$                |
| Beta emission ( $\beta$ )       | ${}_{-1}^0e$      | ${}_0^1n \rightarrow {}_1^1p + {}_{-1}^0e$ | + 1            | 0           | $\frac{N}{Z}$ too large |
| Positron emission ( $\beta^+$ ) | ${}_1^0e$         | ${}_1^1p \rightarrow {}_0^1n + {}_1^0e$    | — 1            | 0           | $\frac{N}{Z}$ too small |
| Electron capture* (E.C.)        | X rays            | ${}_1^1p + {}_{-1}^0e \rightarrow {}_0^1n$ | — 1            | 0           | $\frac{N}{Z}$ too small |
| Gamma emission ( $\gamma$ )     | ${}_0^0\gamma$    | —                                          | 0              | 0           | Excited nucleus         |

(N = neutrons, Z = atomic number)

\*Also called *K* capture—an electron from the *K*-shell ( $n = 1$ ) is captured by the nucleus

- $\beta$ -rays are the same as cathode-rays but  $\beta$ -electrons travel with much higher speeds than the cathode-ray electrons. Also the velocity of cathode-ray electrons is constant while the  $\beta$ -electrons have a wide velocity range.
- Emission of  $\alpha$ - and  $\beta$ -radiations do not cause health hazard to a greater extent due to their low penetrating power (see Table 5.2).
- $\gamma$ -rays are extremely penetrating and represent a greater health hazard to those who work with radioactive chemicals:  
Characteristics of  $\alpha$ -,  $\beta$ - and  $\gamma$ -radiations are summarised in Table 5.2

Table 5.2 Properties of Alpha, Beta and Gamma Rays

| Type               | Alternate name                             | Charge                                                 | Mass   | Speed ( $\text{ms}^{-1}$ ) | Penetrating power                                      | Stopped by     |
|--------------------|--------------------------------------------|--------------------------------------------------------|--------|----------------------------|--------------------------------------------------------|----------------|
| Alpha ( $\alpha$ ) | Helium nucleus<br>(2 protons + 2 neutrons) | +2<br>(deflection towards -ve plate in electric field) | $4m_H$ | $2 \times 10^7$            | Low<br>$\left(\frac{1}{100} \text{ mm of Al}\right)$   | Air or paper   |
| Beta ( $\beta$ )   | Electron                                   | -1<br>(deflection towards +ve plate in electric field) | $m_e$  | $2 \times 10^8$            | Medium<br>$\left(\frac{1}{10} \text{ mm of Al}\right)$ | Thin aluminium |
| Gamma ( $\gamma$ ) | High energy electro-magnetic radiation     | 0<br>(no effect in electric or magnetic field)         | 0      | $3 \times 10^8$            | High<br>25 cm of steel/ 5 cm of lead                   | Thick lead     |
| Positron           | Positive electron                          | +1                                                     | $m_e$  | —                          | Medium                                                 | Thin aluminium |

**Illustration 1** Write balanced nuclear equations for each of the following:

- $\alpha$ -emission from curium-242
- $\beta$ -emission from magnesium-28
- positron emission from xenon-118

**Solution** The key to writing nuclear equations is to make sure that the number of nucleons is the same on both sides of the equation and that the number of elementary and nuclear charges is the same.

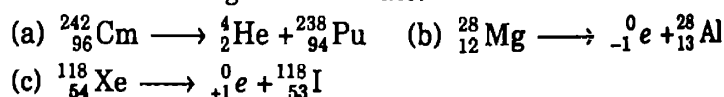


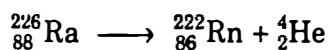
Table 5.3 Distinction between a Radioactive Change and a Chemical Change

| Radioactive change                                                                                                 | Chemical change                                                                                                                                                                                                |
|--------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| (1) New elements are produced<br>${}_{88}^{226}\text{Ra} \longrightarrow {}_{86}^{222}\text{Rn} + {}_2^4\text{He}$ | (1) One compound can be converted to other<br>$\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$                                                                                                    |
| (2) It is irreversible<br>${}_{86}^{222}\text{Rn} + {}_2^4\text{He} \xrightarrow{x}$                               | (2) It can be reversible or irreversible<br>$\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$                                                                                                         |
| (3) Rate of a reaction is independent of imposed external conditions like temperature, pressure, etc.              | (3) Rate is affected by change in temperature, pressure etc.                                                                                                                                                   |
| (4) It is spontaneous and needs not be initiated by external means                                                 | (4) It is made spontaneous by external source as heat, pressure<br>$2\text{H}_2\text{O} \xrightarrow{\text{Heat}} 2\text{H}_2 + \text{O}_2$<br>$\text{C} + \text{O}_2 \xrightarrow{\text{Ignite}} \text{CO}_2$ |
| (5) Large amount of heat is liberated about one million times greater than that liberated in a chemical change.    | (5) Change may be exothermic or endothermic. Heat change is generally very low.                                                                                                                                |

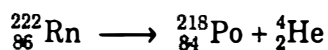
## Radio Elements and the Periodic Table

Elements formed due to emission of  $\alpha$ - and  $\beta$ -particles are placed in groups other than parent element. This is by Soddy and Fajan's group displacement law (1913).

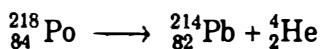
- When an  $\alpha$ -particle is emitted by a radioactive atom, the product has an atomic number two units less than that the parent element and it occupies a position two places to the left of the parent element in the Periodic Table.



II A                  Zero



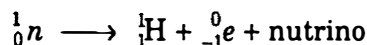
Zero                  VIA



VIA                  IVA

- When a  $\beta$ -particle is emitted by a radioactive atom, the atomic number of the product becomes one unit greater than that of its parent; the product occupies a position one place to the right of the parent element in the Periodic Table.

$\beta$ -emission involves the conversion of a neutron into proton and electron



The electron escapes the atom as  $\beta$ -particle, leaving one proton extra in the nucleus, due to which atomic

number increases by one unit. The neutrinos are energy particles.

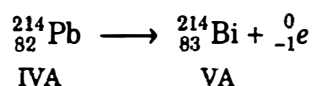
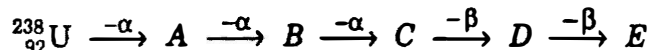


**Illustration 1** Elements with atomic number 89 to 103 all have been placed in group IIIB (actinides). What are the groups of the elements formed in the following disintegration?



**Solution**  ${}_{92}^{238}\text{U}$  belongs to actinide series hence, is of IIIB. Other elements are placed in the groups as shown:

| Elements | Atomic Number | Group                |
|----------|---------------|----------------------|
| A        | 90            | IIIB                 |
| B        | 88            | IIA (alkaline-earth) |
| C        | 86            | Zero (noble gas)     |
| D        | 87            | IA (alkali)          |
| E        | 88            | IIA (alkaline-earth) |

## Units of Radioactivity

Various types of units are used for the radioactivity, each one named after the scientist using it. These are summarised in Table 5.4.

Table 5.4 Units of Radioactivity

| Name       | Symbol       | Defined to be                                                                 | Quantity measured |
|------------|--------------|-------------------------------------------------------------------------------|-------------------|
| Curie      | Ci           | $3.7 \times 10^{10}$ disintegration per second (dps)                          | Decay events      |
| Rutherford | Ru           | $1 \times 10^6$ dps                                                           | Decay events      |
| Becquerel  | Bq (SI unit) | 1 dps                                                                         | Decay events      |
| Gray       | Gy           | 1 kg tissue receiving 1 J of energy                                           | Energy absorbed   |
| Rad        | Rad          | 1 rad = 0.01 Gy                                                               | Energy absorbed   |
| Sievert    | Sv           | gray $\times$ quality number of radiation (e.g., 20 for alpha and 1 for beta) | Tissue damage     |
| Rem        | Rem          | 1 rem = 0.01 Sv                                                               | Tissue damage     |

$$1 \text{ millicurie (mCi)} = 3.7 \times 10^7 \text{ dps}$$

$$1 \text{ microcurie (}\mu\text{Ci)} = 3.7 \times 10^4 \text{ dps}$$

$$1 \text{ Ci} = 3.7 \times 10^{10} \text{ Bq} = 37 \text{ GBq} \text{ (G = giga, } 1 \text{ G} = 10^9)$$

**Specific activity of a radionuclide is its activity per kilogram (or  $\text{dm}^3$ ) of the radioactive material.**

(In some cases specific activity can also be taken as the activity per gram)

## Theory of Radioactive Disintegration

According to this theory (Rutherford, 1903) the atoms of a radioactive element are inherently unstable. They disintegrate spontaneously, emitting  $\alpha$ - or  $\beta$ -particles, and resulting in the formation of a new element which is physically and chemically different from its parent element. The new element formed may, in turn, be again radioactive and will disintegrate in a similar fashion. The process will continue until the atoms of stable element are reached. Following radioactive disintegration series have been identified among the naturally occurring radioactive elements and are summarised in Table 5.5. **Series is decided by dividing the atomic mass of the parent element by 4. Series will be  $(4n + x)$ , where  $x$  is the remainder.**

Neptunium series is artificial series while the other are natural series. The thorium, neptunium and actinium series are so named because an isotope of these elements has the largest half-life in the respective series. The actinium series was once thought to originate with actinium-227—the isotope having the longest half-life amongst the series members. However, it has been investigated that the series actually initiates with a very long-lived uranium-235 isotope.

There is no cross-linking between the four series. Thus, an isotope of one series will not decay to an isotope belonging to another series.

Table 5.5 Radioactive Disintegration Series

|            | Series             | Starts with              | Ends with                |
|------------|--------------------|--------------------------|--------------------------|
| $4n$       | – Thorium series   | ${}^{232}_{90}\text{Th}$ | ${}^{208}_{82}\text{Pb}$ |
| $(4n + 1)$ | – Neptunium series | ${}^{241}_{94}\text{Pu}$ | ${}^{209}_{83}\text{Bi}$ |
| $(4n + 2)$ | – Uranium series   | ${}^{238}_{92}\text{U}$  | ${}^{206}_{82}\text{Pb}$ |
| $(4n + 3)$ | – Actinium series  | ${}^{235}_{92}\text{U}$  | ${}^{207}_{82}\text{Pb}$ |

**Illustration 1** In Table 5.5, four disintegration series have been given. Calculate number of  $\alpha$ - and  $\beta$ -particles emitted in each series.

### Solution

| Series                        | Net disintegration reaction                                     | Number of particles |         |
|-------------------------------|-----------------------------------------------------------------|---------------------|---------|
|                               |                                                                 | $\alpha$            | $\beta$ |
| $4n$ – Thorium series         | ${}^{232}_{90}\text{Th} \longrightarrow {}^{208}_{82}\text{Pb}$ | 6                   | 4       |
| $(4n + 1)$ – Neptunium series | ${}^{241}_{94}\text{Pu} \longrightarrow {}^{209}_{83}\text{Bi}$ | 8                   | 5       |
| $(4n + 2)$ – Uranium series   | ${}^{238}_{92}\text{U} \longrightarrow {}^{206}_{82}\text{Pb}$  | 8                   | 6       |
| $(4n + 3)$ – Actinium series  | ${}^{235}_{92}\text{U} \longrightarrow {}^{207}_{82}\text{Pb}$  | 7                   | 4       |

## Rate of Radioactive Disintegration

Radioactive decay law states :“The rate of disintegration of a radioactive material (the decay rate) is directly proportional to the number of atoms present.”

$$\therefore -\frac{dN}{dt} \propto N$$

$$-\frac{dN}{dt} = \lambda N$$

where  $-\frac{dN}{dt}$  represents rate of decay in disintegration of atoms per unit time (say second),  $N$  the number of atoms disintegrating at that time and  $\lambda$  the disintegration constant (also called decay constant).

$$\lambda = \frac{\text{rate of decay}}{N}$$

Radioactive decay is a **first-order process**.\*

If  $N_0$  is the number of atoms at the start of decay and  $N$  the number of atoms at a given time then by first order kinetics,

$$-\int \frac{dN}{N} = \lambda \int dt$$

$$\lambda = \frac{2.303}{t} \log_{10} \left( \frac{N_0}{N} \right)$$

$$N = N_0 e^{-\lambda t}$$

If  $T_{50}$  (or  $t_{1/2}$ , both notations have been used in further parts) is the half-life which is the time for half of the substance to disappear.

thus, at

$$t = t_{1/2}, N = \frac{N_0}{2} \text{ then } \lambda = \frac{2.303}{t_{1/2}} \log 2$$

$$\therefore t_{1/2} = \frac{2.303 \log 2}{\lambda} = \frac{0.693}{\lambda}$$

Thus, half-life period is independent of number of atoms present at a given time.

Half-life provides an easy way to estimate the time required before a radioactive element is no longer a health hazard. Strontium-90, for example, is a  $\beta$ -emitter with a half-life of 29.1 years. Significant quantities of strontium-90 were dispersed into the environment in atmospheric nuclear bomb tests in the 1960s and 1970s, and from the half-life, we know that a little less than half is still around. Sr-90 is taken into the body and deposited in bone, taking the place of calcium. Radiation damage by Sr-90 in bone has been directly linked to bone-related cancers.

$$\text{If } y = \frac{t}{t_{1/2}} = \text{number of half-lives in a time } t$$

$$\text{then } N = N_0 \left( \frac{1}{2} \right)^y$$

$$\text{and in concentration terms } C = C_0 \left( \frac{1}{2} \right)^y$$

The average-life period ( $t_{av}$ ) is related to  $t_{1/2}$  and disintegration constant by equation:

$$t_{av} = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693} = 1.443 t_{1/2}$$

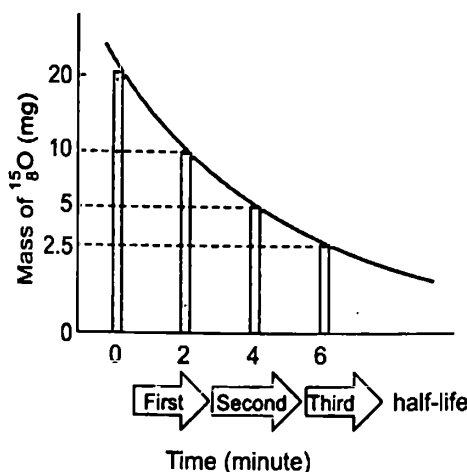


Fig. 5.1 Decay of 20.0 mg of oxygen-15. After each half-life period of 2.0 min, the mass of oxygen-15 decreases by one half

**Illustration 1** Phosphorus-32, a radioactive isotope used in leukemia-therapy has a half-life of 14.28 days. What per cent of a sample disintegrated after 35.0 days?

**Solution** Let sample initially present =  $N_0$

and after 35.0 days sample =  $N$

$$\text{decay constant } \lambda = \frac{0.693}{T_{50}} = \frac{0.693}{14.28} = 0.0485 \text{ day}^{-1}$$

$$\lambda = \frac{2.303}{t} \log \frac{N_0}{N}$$

$$0.0485 = \frac{2.303}{35} \log \frac{N_0}{N}$$

$$\therefore \log \frac{N_0}{N} = \frac{35 \times 0.0485}{2.303} = 0.7375$$

$$\frac{N_0}{N} = 5.464$$

$$\frac{N}{N_0} = 0.183$$

$$\% \text{ of sample left} = 0.183 \times 100 = 18.3$$

$$\begin{aligned} \% \text{ of sample disintegrated} &= 100 - 18.3 \\ &= 81.7\% \end{aligned}$$

#### Alternate Method

Let initial amount of sample =  $N_0 = 100$

and sample left after time  $t = N$

$$\text{then } N = N_0 \left( \frac{1}{2} \right)^y$$

$$\text{where } y = \frac{\text{total time } (t)}{T_{50}} = \frac{35.0}{14.28} = 2.451$$

$$N = 100 \left( \frac{1}{2} \right)^{2.451} = 18.3\%$$

$$\begin{aligned} \therefore \text{Sample disintegrated} &= N_0 - N = 100 - 18.3 \\ &= 81.7\% \end{aligned}$$

**Illustration 2** The decay constant for sodium-24, a radioisotope used medically in blood-study, is  $4.63 \times 10^{-2} \text{ h}^{-1}$ . What is the half-life of  $^{24}\text{Na}$ ?

**Solution** Half-life ( $T_{50}$ ) is related to the decay constant  $\lambda$  of the radioactive disintegration (which follows first-order kinetics) by equation

$$T_{50} = \frac{0.693}{\lambda}$$

$$\therefore T_{50} = \frac{0.693}{4.63 \times 10^{-2} \text{ h}^{-1}} = 14.97 \text{ h}$$

The half-life of sodium-24 is 14.97 h

**Illustration 3** The half-life of radon-222, a radioactive gas of concern as a health hazard is 3.823 days. What is the decay constant when it undergoes first-order radioactive disintegration?

**Solution** As given in above example

$$T_{50} = \frac{0.693}{\lambda}$$

or

$$\begin{aligned} \lambda &= \frac{0.693}{T_{50}} = \frac{0.693}{3.823} \text{ days}^{-1} \\ &= 0.181 \text{ day}^{-1} \end{aligned}$$

## Radioactive Equilibrium

According to the theory of radioactive disintegration, the product of a radioactive disintegration may also be radioactive, and the rate of disintegration of the daughter element depends upon the amount of it present at different time. When steady state is reached

$$\left( \frac{dN}{dt} \right)_{\text{parent}} = \left( \frac{dN}{dt} \right)_{\text{daughter}}$$

or

$$\lambda_1 N_1 = \lambda_2 N_2$$

where  $\lambda_1$  and  $\lambda_2$  are the disintegration constants for the decay of parent and daughter radioactive species and  $N_1$  and  $N_2$  are the number of atoms disintegrating at a given time.

Thus,

$$\frac{N_1}{N_2} = \frac{\lambda_2}{\lambda_1} = \frac{t_1 (\text{half-life})}{t_2 (\text{half-life})}$$

If the parent (say A) has smaller  $\lambda$  than the daughter (B), but none are very small, a steady state is reached at a stage when

$$\frac{N_B}{N_A} = \frac{\lambda_A}{\lambda_B - \lambda_A}$$

This is called a **transient equilibrium**, which is in fact a steady state.

**Illustration 1** Radioactive equilibrium is set up between uranium and radium atoms in a uranium mineral in the ratio of 28 : 1.  $T_{50}$  for radium is 1620 years. Calculate the disintegration constant of uranium.

**Solution** When radioactive equilibrium is set up

$$\lambda_1 N_1 = \lambda_2 N_2$$



$$\frac{\lambda_U}{\lambda_{Ra}} = \frac{N_{Ra}}{N_U}$$

$$\frac{\lambda_U}{0.693} = \frac{1}{28}$$

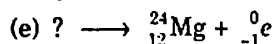
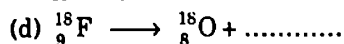
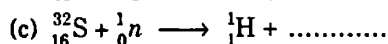
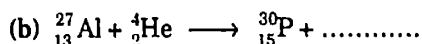
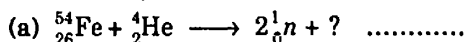
$$\frac{\lambda_U}{(T_{50})_{Ra}} = \frac{1}{28}$$

$$\therefore \lambda_U = \frac{1}{28} \times \left( \frac{0.693}{1620 \text{ years}} \right)$$

$$= 1.528 \times 10^{-6} \text{ yr}^{-1}$$

## Target Practice 1

1. Complete the following nuclear equations. Write the mass number and atomic number for the remaining particle, as well as its symbol.



2. What particle is emitted in the following nuclear reactions?

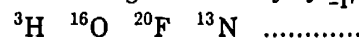
(a) Gold-198 decays to mercury-198

(b) Radon-222 decays to polonium-218

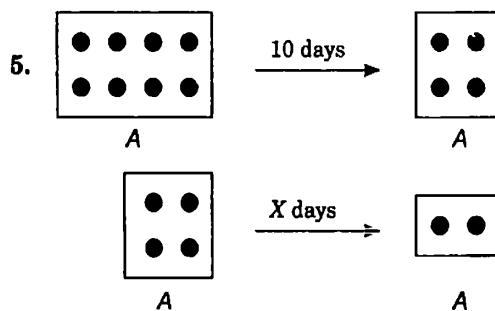
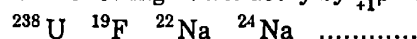
(c) Cesium-137 decays to barium-137

(d) Indium-110 decays to cadmium-110

3. Which of the following nuclei decay by  ${}^0_{-1}\beta$  decay?



4. Which of the following nuclei decay by  ${}^0_{+1}\beta$  decay?



Specify X .....

## Answers

1. (a)  ${}^{56}_{28}\text{Ni}$  (b)  ${}^1_0n$  (c)  ${}^{32}_{15}\text{P}$  (d)  ${}^0_1e$  (e)  ${}^{24}_{11}\text{Na}$
2. (a)  ${}^{198}_{79}\text{Au} \longrightarrow {}^{198}_{80}\text{Hg} + {}^0_{-1}e$
- (b)  ${}^{222}_{86}\text{Rn} \longrightarrow {}^{218}_{84}\text{Po} + {}^4_2\text{He}$
- (c)  ${}^{137}_{55}\text{Cs} \longrightarrow {}^{137}_{56}\text{Ba} + {}^0_{-1}e$
- (d)  ${}^{110}_{49}\text{In} \longrightarrow {}^{110}_{48}\text{Cd} + {}^0_{+1}e$

3. Refer text

4. Refer text

5.  $X = 10$  (Half-life of first-order disintegration is independent of initial radioactivity)

## Practice Exercise 1

1. Although a neutron within a nucleus is stable, a neutron in free space decays into a proton and an electron ( $\beta$ -particle). Write its equation.

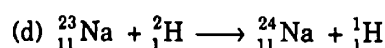
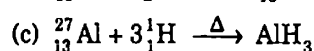
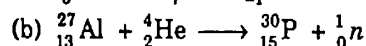
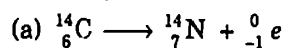
2. What are approximate atomic weight of electron and positron per mol?

3.  ${}^{234}_{90}\text{Th}$  disintegrates to give  ${}^{206}_{82}\text{Pb}$  as the final product. How many  $\alpha$ - and  $\beta$ -particles are emitted during the process?

4. Fill in the blanks :

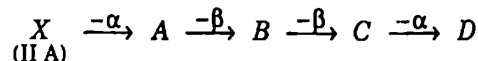
- (a) Alpha-rays are fast moving ..... nuclei.
- (b) Emission of one  $\alpha$ - and two  $\beta$ -particles will result in the formation of ..... .
- (c) ..... rays cause health hazards to maximum extent.
- (d) Nuclear fusion is a ..... reaction.
- (e) A radioactive change is always ..... .
- (f) The rate of radioactive change is independent of pressure and ..... .
- (g) New elements are produced in ..... .

5. Identify chemical change and radioactive change in the following :



6.  ${}^{238}_{92}\text{U}$  (group III B) emits one  $\alpha$  particle. What is the group of new element formed?

7. Assign groups to the elements A, B, C, D and E starting from element X (group II A)



What is relation between A and D?

What is relation between A, B and C?

8. If a radioactive element  ${}_{79}\text{Au}$  emits  $\beta$ -particle, what is the new group? Is there any change in the number of moles of daughter element?  ${}_{79}\text{Au}$  belongs to group I B (copper family).

9. What is relation between following units:  
 (a) Bq and Ci (b) Bq and Ru  
 (c) Ru and Ci
10.  $\left(-\frac{dN}{dt} = \lambda N\right)$  represents the rate of decay in disintegration of atoms per unit time, where  $N$  is the number of atoms disintegrating at that time and  $\lambda$  the disintegration constant. Calculate number of curies when number of atoms equal to one Avogadro's number disintegrates in the case when  $\lambda = 0.6146 \times 10^{-10} \text{ s}^{-1}$ .

1.  ${}^1_0n \longrightarrow {}^1_1p + {}^0_{-1}\beta$
2. atomic weight of electron or positron  
 $= 9.1 \times 10^{-28} \times 6.00 \times 10^{23} \text{ g mol}^{-1} = 5.48 \times 10^{-4} \text{ g mol}^{-1}$
3.  $7\alpha$  and  $6\beta$
4. (a) helium; (b) an isotope; (c)  $\gamma$  (d) thermonuclear  
 (e) spontaneous (f) temperature (g) radioactive change.
5. (a), (b) and (d) radioactive change; (c) chemical change.
6. III B ( $Z = 90$  to  $104$  are in III B)
7. A (Zero), B (IA), C (IIA), D (Zero)  
 A and D are isotopes;  
 A, B and C are isobars.

## Answers

11. The decay constant for mercury-197, a radioisotope used medically in kidney-scans, is  $1.08 \times 10^{-2} \text{ h}^{-1}$ . What is the half-life of mercury-197?
12. The half-life of carbon-14 is 5715 yr. What is decay constant?
13. Write balanced nuclear equations for each of the following :  
 (a)  $\beta$ -emission from ruthenium-106  
 (b)  $\alpha$ -emission from bismuth-189  
 (c) electron capture by polonium-204.

8.  ${}^{79}_{47}\text{Au} \longrightarrow {}^{80}_{80}\text{Hg} + \beta^-$ .  ${}^{80}_{80}\text{Hg}$  belongs to II B. (zinc family)  
 There is no change in number of moles since atomic mass remains unchanged.
9. (a)  $1 \text{ Ci} = 3.7 \times 10^{10} \text{ Bq}$  (b)  $1 \text{ Bq} = 1 \times 10^6 \text{ Ru}$   
 (c)  $1 \text{ Ci} = 3.7 \times 10^4 \text{ Ru}$
10. 1000 Ci 11. 64.17 h 12.  $1.212 \times 10^{-4} \text{ yr}^{-1}$
13. (a)  ${}^{106}_{44}\text{Ru} \longrightarrow {}^0_{-1}e + {}^{106}_{45}\text{Rh}$   
 (b)  ${}^{189}_{83}\text{Bi} \longrightarrow {}^4_2\text{He} + {}^{185}_{81}\text{Tl}$   
 (c)  ${}^{204}_{84}\text{Po} + {}^0_{-1}e \longrightarrow {}^{204}_{83}\text{Bi}$

## Nuclear Stability

A number of basic questions have probably occurred to you as we have been describing nuclear decay processes.

Why do some radioactive nuclei decay by  $\alpha$ -emission and some by  $\beta^-$ -emission?

Why do the lighter elements have so few naturally occurring radioactive nuclides, whereas those of the heavier elements all seem to be radioactive?

From the Fig. 5.2, it is clear that nuclides with even number of protons and neutrons have higher binding energies than their neighbours and are stable. Experimentally, it is found that nuclei with certain number of protons or neutrons appear to be very stable. These numbers called **magic numbers** and associated with specially stable nuclei, were later explained by the shell model. According to this theory, a **magic number** is the number of nuclear particles in a completed shell of protons or neutrons.

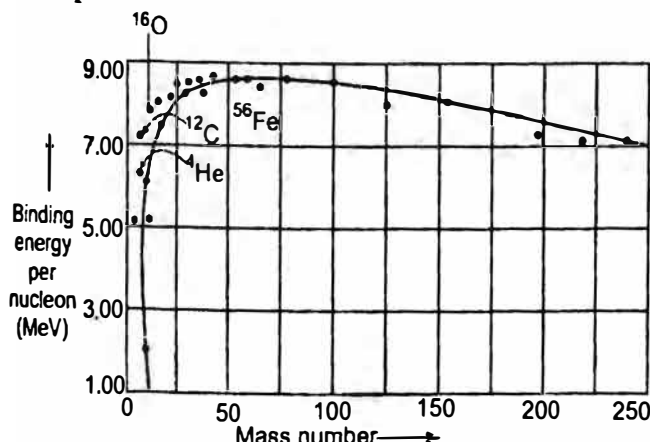
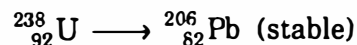


Fig. 5.2 Binding energy per nucleon

- Magic number for protons : 2, 8, 20, 28, 50, 82, 114
- Magic number for neutrons : 2, 8, 20, 28, 50, 82, 126
- ${}^4_2\text{He}$  ( $\alpha$ -particle) is stable. It contains two protons and two neutrons hence, it contains magic number of protons (2), neutrons (2).



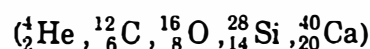
It ( ${}^{206}_{82}\text{Pb}$ ) has 82 protons (magic number)

Table 5.6 gives number of stable isotopes.

Table 5.6 Number of Stable Isotopes with Even and Odd Numbers of Protons and Neutrons

|                    | Number of stable isotopes |      |      |     |
|--------------------|---------------------------|------|------|-----|
|                    | 157                       | 52   | 50   | 5   |
| Number of protons  | Even                      | Even | Odd  | Odd |
| Number of neutrons | Even                      | Odd  | Even | Odd |

- Finally when we plot each stable nuclide on a graph between the number of protons ( $Z$ ) and the number of neutrons ( $N$ ), these stable nuclides fall in a certain region, or band, of graph. (Fig. 5.3). The **band of stability** is the region in which stable nuclides lie in a plot of number of protons against number of neutrons. From this graphs it is clear that
- Stable nuclei are those for which number of neutrons and protons are equal and are generally upto 20.



- For higher atomic numbers, because of increasing repulsive forces between protons, large number of

neutrons must be present to stabilise a nucleus and the neutron/proton ( $n/p$ ) ratio increases.

For bismuth the ratio is about 1.5 : 1

- Isotopes of all the known elements with  $Z > 83$  are radioactive.

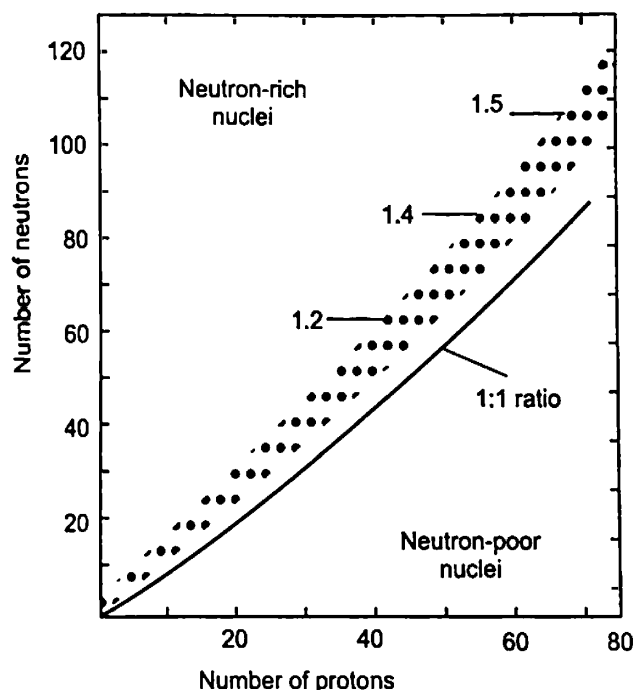
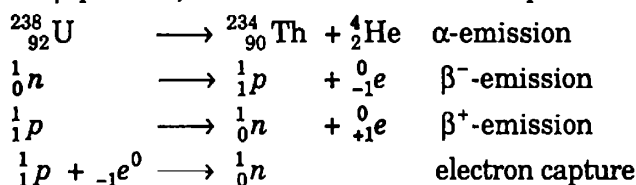


Fig. 5.3 Plot of the number of neutrons against the number of protons in stable nuclei (shown by dots)

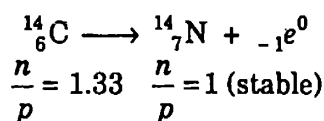
## Mechanism of Radioactive Decay

The emission of an  $\alpha$ -particle by a nucleus is not difficult to visualise. A bundle of four nucleons (two protons, two neutrons) is ejected from a nucleus, and the nucleus becomes energetically more stable. In the emission of  $\beta$ -particle, neutron is converted into proton.



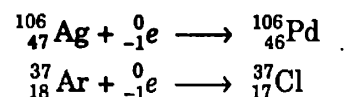
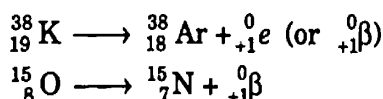
- In general, if a nuclide lies above the belt of stability (Fig. 5.3), the  $\left(\frac{n}{p}\right)$  ratio is too high.

A neutron is converted to a proton and a  $\beta^-$  particle is emitted.



- If a nuclide lies below the belt of stability, the  $\left(\frac{n}{p}\right)$  ratio is too low.

Either a proton is converted to a neutron, followed by  $\beta^+$  emission or electron capture occurs.



- All nuclides with atomic number greater than 83 are beyond the band of stability and are radioactive. Many of these decay by  $\alpha$ -emission.

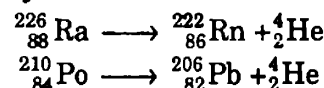
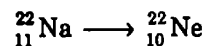


**Illustration 1** Consider the following radioactive change

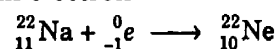


What is the type of particle captured or emitted?

**Solution** 
$${}^{22}_{11}\text{Na} \longrightarrow {}^{22}_{10}\text{Ne}$$

There is change in atomic number of one unit, hence, it can

- (i) capture an electron



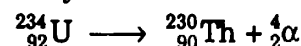
- (ii) emit a positron 
$${}^{22}_{11}\text{Na} \longrightarrow {}^{22}_{10}\text{Ne} + {}^0_{+1}\beta$$

**Illustration 2** Identify probable mode(s) of decay for each isotope and write an equation for the decay process.

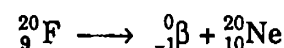
- (a) oxygen-15,  ${}^{15}_8\text{O}$  (b) uranium-234  ${}^{234}_{92}\text{U}$  (c) fluorine-20,  ${}^{20}_9\text{F}$  (d) manganese-56,  ${}^{56}_{25}\text{Mn}$

**Solution** (a) Oxygen-15 has 7 neutrons and 8 protons, so the  $n/p$  ratio is less than 1-too low for  ${}^{15}_8\text{O}$  to be stable. Nuclei with too few neutrons are expected to decay by either positron emission or electron capture. In this instance, the process is  ${}^0_{+1}\beta$  emission, and the equation is 
$${}^{15}_8\text{O} \longrightarrow {}^0_{+1}\beta + {}^{15}_7\text{N}.$$

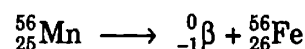
- (b) Alpha emission is a common mode of decay for isotopes of elements with atomic numbers higher than 83. The decay of uranium-234 is one example.



- (c) Fluorine-20 has 11 neutrons and 9 protons, a high  $n/p$  ratio. The ratio is lowered by  $\beta$  emission :



- (d) The atomic weight of manganese is 54.85. The higher mass number, 56, suggests that this radioactive isotope has an excess of neutrons, in which case it would be expected to decay by  $\beta$ -emission :



## Nuclear Reactions

We may classify nuclear reactions according to the projectiles as :

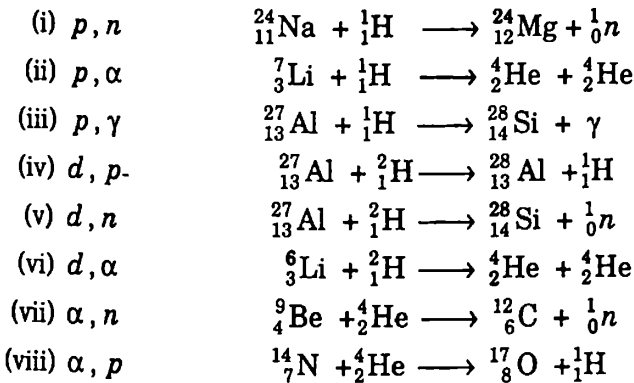
### Charged Particle Reactions

Such reactions may be carried out by accelerated protons, deuterons or alpha particles:

| Projectile     | Reaction type                              |
|----------------|--------------------------------------------|
| Proton         | $(p, n), (p, \alpha), (p, \gamma), (p, d)$ |
| Deuteron       | $(d, p), (d, n), (d, \alpha), (d, \gamma)$ |
| Alpha particle | $(\alpha, n), (\alpha, p)$                 |

- By writing  $(p, n)$ , it means, proton is absorbed and neutron is emitted.

Examples :

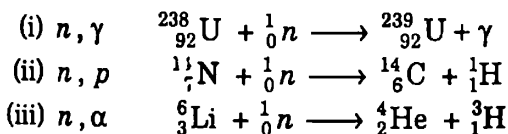


- Reaction (ii) is the first artificial nuclear reaction carried out with artificially accelerated particles.
- Reaction (vi) gives one of the highest non-fission energies (22.2 MeV) recorded for light atoms.
- Neutron was discovered through the reaction (vii).
- Reaction (viii) is the first artificial nuclear reaction studied.

## Neutral Particle Reactions

Neutrons are generally used as projectiles in such reactions. Neutrons of high energy are obtained from different artificial nuclear reactions. These are slowed down through **moderators** like graphite, heavy water, paraffin, etc. Much of the energies of the neutron is transferred to these substances through elastic scattering.

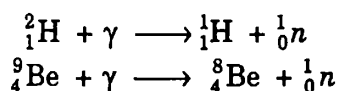
Example :



- Reaction (i) shows the formation of transuranium elements.

Reaction (iii) shows the production of tritium.

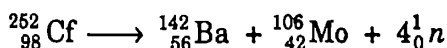
Reactions initiated by photons may also be considered as neutral particle reactions.



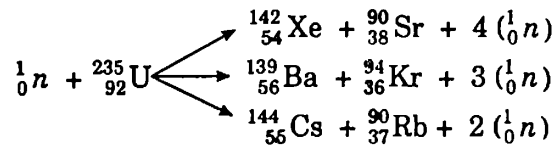
## Nuclear Fission

It is a nuclear reaction in which a heavy nucleus splits into lighter nuclei and energy is released.

- Californium -252 decays both by alpha emission (97%) and by spontaneous fission (3%). During spontaneous fission, the nucleus splits into two stabler, lighter nuclei plus several neutrons.



- When a neutron strikes the  ${}_{92}^{235}\text{U}$  nucleus, the nucleus splits into roughly equal parts, giving off several neutrons.



- If the neutrons from each nuclear fission are absorbed by other uranium -235 nuclei, these nuclei split and release even more neutrons. Thus, a **chain reaction can occur**. A *nuclear chain reaction* is a self-sustaining series of nuclear fissions caused by the absorption of neutrons released from previous nuclear fissions. This is shown in Fig. 5.4.

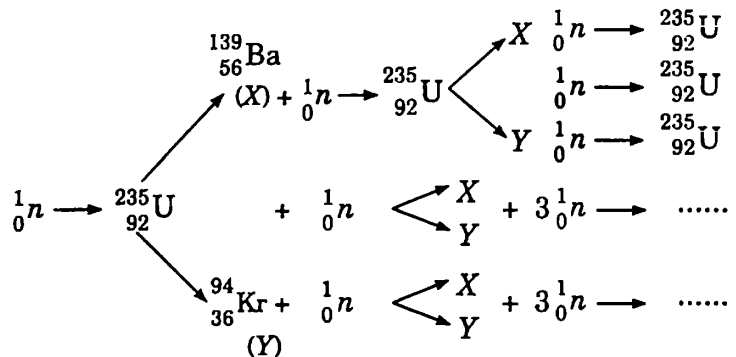


Fig. 5.4 Representation of nuclear chain reaction of nuclear fissions

- There should be a **critical size** of the fissionable material to maintain a fission chain. This in turn, requires a minimum **critical mass** of the fissionable material. It is the *smallest mass of the fissionable material in which a chain reaction can be sustained*. If the mass is much larger than this (a supercritical) mass, the number of nuclei that split multiply rapidly. An *atomic bomb is detonated with a small amount of chemical explosive that pushes together two or more masses of fissionable material to get a supercritical mass*.

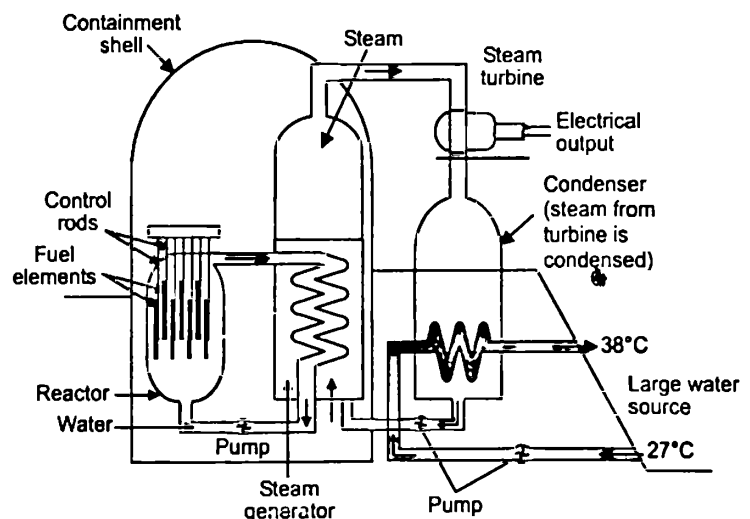
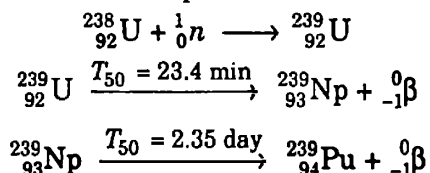


Fig. 5.5 A diagram of a nuclear power plant. Heat produced in the reactor core is transferred by coolant circulating in a closed loop to a steam generator, and the steam then drives a turbine to generate electricity.

A nuclear fission reactor (Fig. 5.5) is a device that permits a controlled chain nuclear-fissions. **Control rods** made of elements such as boron and cadmium, absorb additional neutrons and can therefore, slow the chain reactions.

A nuclear reactor consists of three components:

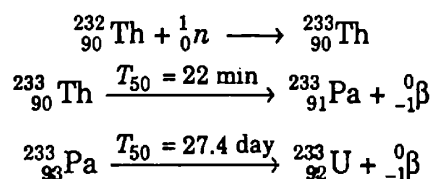
- A fissile material (uranium enriched in  $^{235}_{92}\text{U}$ , say 2.3%)
  - A moderator (graphite or heavy water  $\text{D}_2\text{O}$ ) to slow the neutrons so that they are captured and become effective to bring about fission reaction.
  - Control rods made of boron steel or cadmium, which are capable of absorbing neutrons and are used to ensure that neutron flux is under control and thus chain-reaction is controlled. The large amount of energy released from the fission is used for steam generation through heat exchanges to produce electricity. At present our country is proud of having more than 12 such nuclear power plants producing electricity.
- A **breeder reactor** uses uranium fuel, but unlike a conventional nuclear reactor, it produces more fissionable materials than it uses. When uranium-238 is bombarded with fast neutrons, the following reactions take place:



In this manner the non-fissionable uranium-238 is transmuted into the fissionable isotope plutonium-239.

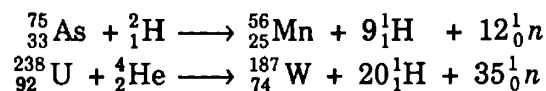
In a typical breeder reactor, nuclear fuel containing uranium-235 or plutonium-239 is mixed with uranium-238 so that breeding takes place within the core. For every uranium-235 (or plutonium-239) nucleus undergoing fission, more than one neutron is captured by uranium-238 to generate plutonium-239. Thus, the amount of fissionable material can be steadily increased as the starting nuclear fuels are consumed.

$^{232}_{90}\text{Th}$  is also used. When it captures slow neutrons, it is transmuted to uranium-233 which is also a fissionable isotope.



## Spallation

Seaborg and his coworkers (1947) observed that bombardment with high energy charged particles (e.g., 400 MeV protons or 200 MeV deuterons) can break some target nuclei into several smaller nuclei with the emission of a large number of nucleons (10 to 20 or more). These are called spallation reactions.



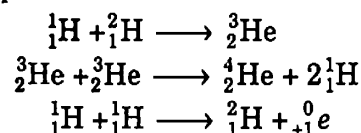
## Nuclear Fusion

In this type of nuclear reaction, certain light nuclei may fuse together with the liberation of tremendous amount of energy. To achieve this, the colliding nuclei must possess enough kinetic energy to overcome the initial repulsion between the positively charged cores. This energy may be made available by raising the temperature of the reacting system to several million degrees. Such reactions are therefore, also known as **thermonuclear reactions**.



The energy of a fusion process is due to mass defect (converted to binding energy). The high temperature required to initiate such reactions may be attained initially through a fission process.

Spectroscopic evidence indicates that the sun is a tremendous fusion reactor consisting of 73% H, 26% He and 1% other elements. Following fusion reactions are believed to take place:



A major concern in choosing the proper nuclear fusion process for energy production is the temperature necessary to carry out the process. Some promising reactions are:

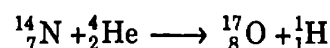
| Reactions                                                                         | Energy released                 |
|-----------------------------------------------------------------------------------|---------------------------------|
| ${}^2_1\text{H} + {}^2_1\text{H} \longrightarrow {}^3_1\text{H} + {}^1_1\text{H}$ | $6.3 \times 10^{-13} \text{ J}$ |
| ${}^2_1\text{H} + {}^3_1\text{H} \longrightarrow {}^4_2\text{He} + {}^1_0n$       | $2.8 \times 10^{-12} \text{ J}$ |
| ${}^6_3\text{Li} + {}^2_1\text{H} \longrightarrow 2{}^4_2\text{He}$               | $3.6 \times 10^{-12} \text{ J}$ |

## Artificial Radioactivity

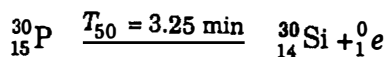
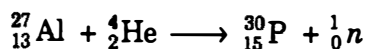
Bombardment of stable elements with high energy  $\alpha$ -particles, protons, neutrons, deuterons or  $\gamma$ -rays produce radioactive nuclides. These radio-nuclides do not occur naturally and may be called man-made or artificial. The radioactivity exhibited by these artificial radio-nuclides is referred to as **artificial radioactivity** or as **induced radioactivity**. (I. Curie and F. Joliot-1934)

The decay resulting from artificial radioactivity is usually a one-step process, i.e., the radioisotope disintegrates into a stable isotope which does not show any further tendency to decay.

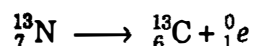
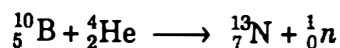
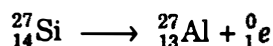
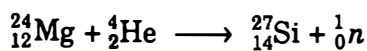
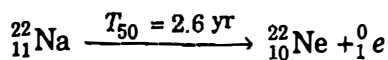
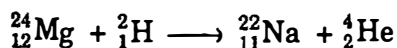
- The first artificial breakdown of the atomic nucleus was achieved by Rutherford in 1919. He bombarded nitrogen with  $\alpha$ -particles and obtained oxygen and protons



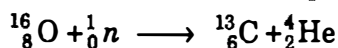
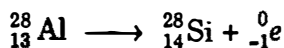
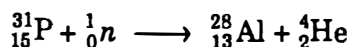
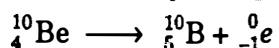
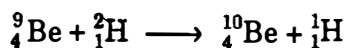
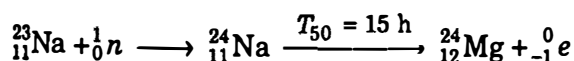
- (b) The newly formed isotope undergoes positron emission.



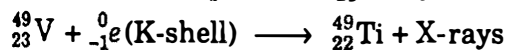
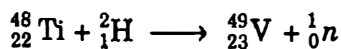
artificial radioactive                  stable



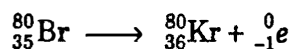
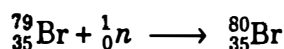
- (c) The newly formed isotope undergoes electron emission ( $\beta$ -decay)



- (d) The newly formed isotope undergoes K-electron capture (electron from K-shell or 1s energy level). In this process energy is emitted in the form of X-rays.



- (e) There can be formation of isomer in artificial nuclear reactions.



Thus  ${}^{80}\text{Br}$  exists as two nuclear-isomers.

## Binding Energy and Packing Fraction

The nearest integer to the mass of a nuclide (in the atomic mass scale) was called the mass number of that isotope. The difference between the actual isotopic mass and mass number was termed as **mass defect** of the nuclide.

Thus,  $\Delta m$  (mass defect) = isotopic mass ( $m$ )  
– mass number ( $A$ )

Aston introduced a term “packing fraction” for each nuclide to compare their mass excess, it was defined as:

$$\text{Packing fraction } (f) = \frac{\Delta m}{A} \times 10^4$$

- The packing fraction does not have any precise theoretical significance but it gives an indication about the stability of the nucleus.
- A negative packing fraction indicates that the isotopic mass is less than the nearest whole number. This suggests that a small fraction of the mass has been converted into energy of formation of that nucleus. **Hence, the more negative the packing fraction of an element, the more stable should be the nucleus.**
- On the other hand, a positive packing fraction indicates that the concerned nucleus should be less stable.
- Generalisations are shown in the Fig. 5.6.

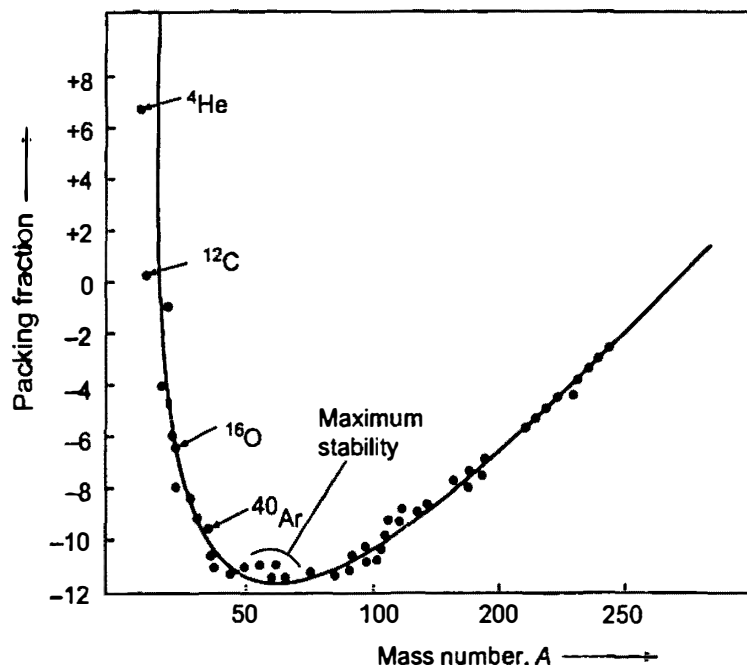


Fig. 5.6 Plot of packing fraction against mass number

This shows:

- The packing fractions of the stable nuclides lie more or less on a smooth curve.
- The curve passes through a minima in the mass number range 50–60, implying the maximum stability.
- After the minima, packing fraction steadily increases and ultimately becomes positive for elements of high mass number.

This is consistent with the observed radioactivity, i.e., inherent instability, of these elements.

$$\text{Binding energy } (B) = \Delta m \times c^2$$

Binding energy of the nucleus is equal to the energy required to split the nucleus into its component nucleons.

Nuclear binding energy is generally expressed in the non-SI unit of MeV (mega electron volt).

$$\text{Since, } 1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$$

$$\therefore (B) \text{ for one amu} = 1.66 \times 10^{-27} \times (3 \times 10^8)^2 \text{ J}$$

$$= \frac{1.66 \times 10^{-27} \times (3 \times 10^8)^2 \text{ J}}{1.602 \times 10^{-19} \text{ J/eV}}$$

$$= 932.6 \times 10^6 \text{ eV} = 932.6 \text{ MeV}$$

$$\therefore (B) = \Delta m (\text{in amu}) \times 931 \text{ MeV}$$

$$\text{Binding energy per nucleon } (\bar{B}) = \frac{B}{A}$$

$$= \frac{\text{total binding energy}}{\text{total number of nucleons}}$$

A plot of average binding energy per nucleon against mass number gives a nearly smooth curve (Fig 5.2). The curve is practically an inversion of the curve obtained by plotting packing fractions (Fig 5.6). Maximum binding energy per nucleon is indicated in the mass number range 55–60. The average binding energies for  ${}^4\text{He}$ ,  ${}^{12}\text{C}$  and  ${}^{16}\text{O}$  lie above the curve, showing that they are exceptionally stable.

This may be attributed to several factors. Firstly these atoms have even-even combination of protons and neutrons in their nuclei.

| Nuclei              | Neutron | Proton |
|---------------------|---------|--------|
| ${}^4_2\text{He}$   | 2       | 2      |
| ${}^{12}_6\text{C}$ | 6       | 6      |
| ${}^{16}_8\text{O}$ | 8       | 8      |

Secondly, number of protons and neutrons are equal. Thirdly the electrostatic repulsion between the protons in these three cases is less than that of their immediate neighbours. Electrostatic repulsion is measured by

$$= \frac{Z^2}{(A)^{1/3}}$$

where  $Z$  is the number of protons and  $A$  the mass number. We compare this type of force with the immediate neighbours.

Table 5.7 Electrostatic Force of Different Nuclei

| Nuclei              | Z | A  | Electrostatic force              |
|---------------------|---|----|----------------------------------|
| ${}^4_2\text{He}$   | 2 | 4  | $\frac{(2)^2}{(4)^{1/3}} = 2.53$ |
| ${}^6_3\text{Li}$   | 3 | 6  | 4.97                             |
| ${}^{12}_6\text{C}$ | 6 | 12 | 15.78                            |
| ${}^{14}_7\text{N}$ | 7 | 14 | 20.33                            |
| ${}^{16}_8\text{O}$ | 8 | 16 | 25.39                            |
| ${}^{19}_9\text{F}$ | 9 | 19 | 30.45                            |

In case of helium-4 and oxygen-16, there is an additional reason for exceptional stability. In each case number of neutrons (2 and 8) corresponds to magic number.

**Note:** To convert amu into MeV conversion factor is generally taken 931.

**Illustration 1** Helium-6 is a radioactive isotope with  $T_{50} = 0.81 \text{ s}$ . Calculate the binding energy if mass defect is  $0.03141 \text{ g mol}^{-1}$ . Also calculate binding energy of helium-4 whose mass defect is  $0.03038 \text{ g mol}^{-1}$ . Is a  ${}^6\text{He}$  nucleus more stable or less stable than a  ${}^4\text{He}$  nucleus?

**Solution** Binding energy of  ${}^6\text{He} = \Delta m \times c^2$

$$= \left( \frac{0.03141}{1000} \text{ kg mol}^{-1} \right) (3 \times 10^8 \text{ ms}^{-1})^2$$

$$= 2.8269 \times 10^{12} \text{ J mol}^{-1}$$

Binding energy of  ${}^4\text{He} = \left( \frac{0.03038}{1000} \text{ kg mol}^{-1} \right) (3 \times 10^8 \text{ m s}^{-1})^2$

$$= 2.7342 \times 10^{12} \text{ J mol}^{-1}$$

Binding energy of  ${}^6\text{He}$  per nucleon =  $\frac{2.8269 \times 10^{12}}{6}$

$$= 4.7115 \times 10^{11} \text{ J per nucleon}$$

Binding energy of  ${}^4\text{He}$  per nucleon =  $\frac{2.7342 \times 10^{12}}{4}$

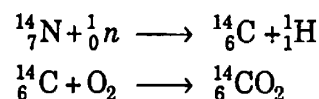
$$= 6.8355 \times 10^{11} \text{ per nucleon}$$

Thus,  ${}^6\text{He}$  nucleus is less stable than a  ${}^4\text{He}$  nucleus.

## Applications of Radioactive Isotopes

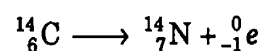
### Carbon-Dating

Radiocarbon-dating of archaeological artifacts depends on the slow and constant production of radioactive carbon-14 in the upper atmosphere by neutron bombardment of nitrogen atoms (The neutrons come from the bombardment of other atoms by cosmic rays).



Carbon-14 atoms produced in the upper atmosphere combine with oxygen to yield  ${}^{14}\text{CO}_2$ , which slowly diffuses into the lower atmosphere, where it mixes with ordinary  ${}^{12}\text{CO}_2$  and is taken up by plants during photosynthesis. When these plants are eaten, carbon-14 enters the food chain and is ultimately distributed evenly throughout all living organisms.

As long as a plant or animal is alive, a dynamic equilibrium exists in which an organism excretes or exhales the same amount of  ${}^{14}\text{C}$  that it takes in and the ratio of  ${}^{14}\text{C}$  to  ${}^{12}\text{C}$  in the living organism is the same as that in the upper atmosphere. When the plant or animal dies, however, it no longer takes in more  ${}^{14}\text{C}$ , and the ratio of  ${}^{14}\text{C}$  to  ${}^{12}\text{C}$  slowly decreases due to decay of  ${}^{14}\text{C}$



Thus, from the activity of  $^{14}\text{C}$  in the dead organism and that of the fresh sample (in the atmosphere), age can be decided.

$$\lambda(\text{decay constant}) = \frac{2.303}{t(\text{age})} \log \frac{N_0 (\text{original activity})}{N (\text{final activity})}$$

$$\text{Also, } \lambda = \frac{0.693}{T_{50}} (\text{half-life})$$

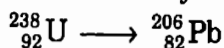
Thus,  $t$  (age) can be determined.

$$\text{or } N = N_0 \left(\frac{1}{2}\right)^y$$

$$\text{where } y = \frac{\text{total time } (t)}{\text{half-life } (T_{50})}$$

### Rock (Geological) Dating

Uranium-238 has a half-life of  $4.46 \times 10^9$  years and decays through a series of events to yield lead-206.



The age of uranium containing rock can, therefore, be determined by measuring the  ${}^{238}\text{U}/{}^{206}\text{Pb}$  ratio.

It is based on the kinetics of radioactive decay. It is assumed that no lead was initially present in the sample and the whole of it came from the uranium.

Initial radioactivity =  $[\text{U}] + [\text{Pb}] = N_0$  in terms of gram atoms

Final radioactivity =  $[\text{U}] = N$

We have assumed that due to high value of  $T_{50}$  of uranium, its amount remains unchanged.

$$\frac{N_0}{N} = \frac{[\text{U}] + [\text{Pb}]}{[\text{U}]} = 1 + \frac{[\text{Pb}]}{[\text{U}]}$$

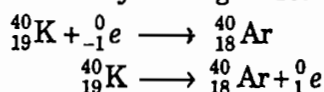
$$\begin{aligned} \text{Thus, } \lambda &= \frac{2.303}{T_{50}} \log \left( \frac{N_0}{N} \right) \\ &= \frac{2.303}{T_{50}} \log \left[ 1 + \frac{[\text{Pb}]}{[\text{U}]} \right] \end{aligned}$$

$$\text{or } \left[ 1 + \frac{[\text{Pb}]}{[\text{U}]} \right] = (2)^y$$

where  $y = \frac{t}{T_{50}}$  hence,  $t$  is calculated.

Thus, knowing the ratio of uranium to lead or thorium to lead in a particular minerals and knowing the half-lives of the radioisotopes, the age of the natural substance may be estimated.

Similarly, potassium-40 has a half-life of  $1.26 \times 10^9$  years and decays through electron capture and through positron emission to yield argon-40.

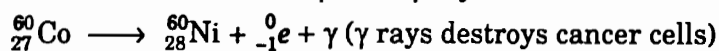


The age of a rock can be determined by crushing a sample, measuring the amount of  ${}^{40}\text{Ar}$  gas that escapes, and comparing the amount of argon-40 with the amount of  ${}^{40}\text{K}$  remaining in the sample

### Medical Uses of Radioactivity

- French physician Henri Danlos first used radium in the treatment of tuberculous skin lesion. Now, uses of radioactivity have become a crucial part of modern medical care, both diagnostic and therapeutic
- Various techniques used in medical treatment are grouped into three classes:
  - (i) *in vivo* procedures,
  - (ii) therapeutic procedures and
  - (iii) imaging procedures.
- *In vivo* studies—those take place inside the body—are carried out to assess the functioning of a particular organ or body system. A radio-pharmaceutical agent is administered, and its path in the body—whether it is absorbed, excreted, diluted or concentrated is determined by analysis of blood or urine samples.  $^{51}\text{Cr}$  radioisotope is used in this type of study.
- Therapeutic procedures—those in which radiation is used as a weapon to kill diseased tissue—can involve either external or internal source of radiation.

**Cobalt-60** used in external radiation therapy for the treatment of cancer. It is embedded in the cancerous tissue and emits both  $\beta$ - and  $\gamma$ -rays



**Sodium-24** injected alongwith salt solution to trace the flow of blood.

**Iodine-131** used in internal radiation therapy for the treatment of thyroid disease.

**Phosphorus-32** used for leukemia therapy which controls *polycythemia vera*—a condition in which the bone marrow produces excess red blood cells. The radioactive P-32 (in the form of phosphate) gets preferentially absorbed in the bone marrow and emits  $\gamma$ -rays, which destroy excessive red blood corpuscles.

- Imaging procedures gives diagnostic information about the health of body organs by analysing the distribution pattern of radioisotopes introduced into the body.

**Iodine-131** employed to study the structure and activity of thyroid glands.

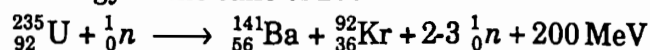
**Iodine-123** used in imaging the brain.

**Technetium-99 M** used in bone scans.

- **MRI** (magnetic resonance imaging) uses radio-waves to stimulate certain nuclei in the presence of an extremely powerful magnetic field.

### Power Generation

The fission of uranium-235 nucleus by slow neutrons, releases energy to the tune of 200 MeV





which may be converted into electrical energy. Power produced by nuclear energy is unmatched as compared to any other energy resource. Theoretically, one tonne of uranium can give as much electrical energy as 3 million tonne of coal or 12 million barrels of oil. Further, not only the reserves of coal and oil are exhausting fastly, but burning of these fossil fuels pollutes the environment. Nuclear energy is a clean and abundant resource for power generation.

## Agricultural Applications

Isotopes can be used to measure the uptake of nutrients. Plants take up phosphorus containing compounds from the soil through their roots. By adding a small amount of radioactive  $^{32}\text{P}$ , a  $\beta$ -emitter (with a half-life of 14.3 days), to a fertiliser and then measuring the rate at which the radioactivity appears in the leaves, plant biologists can determine the rate at which phosphorus is taken up. The outcome can assist agriculture-scientists in identification of hybrid strain of plants that can absorb phosphorus quickly, resulting in faster-maturing crops, better yields per acre, and more food or fibre at lower cost. To measure pesticide level, a pesticide can be tagged with a radioisotope and then applied to a test field. By counting the disintegrations of radioactive tracer, information can be obtained about how much pesticide is in soil; is taken up by the plant, and is carried off in runoff surface water. **(Radioactive isotope used to carry out these investigation has short half-life and decays to harmless levels in a few days)**

**Isotopes Dilution Technique** is used to determine, the volume of blood in an animal subject. A small amount of radioactive isotope is injected into the bloodstream. After a period of time to allow the isotope to become distributed throughout the body, a blood sample is taken and its radioactivity measured.

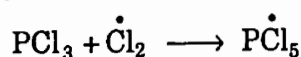
## Chemical Investigation

### Structural Determination

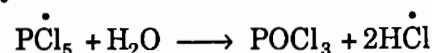
When more than one atom of a particular element are present in a molecule, it needs to be decided whether all of these are equivalent or not. Radioisotope labelling settles the issue.

- To decide nature of bonding in  $\text{PCl}_5$ .

In order to determine whether all five chlorides in phosphorus (V) chloride are in a chemically similar environment, the compound may be synthesised using labelled chlorine molecules.



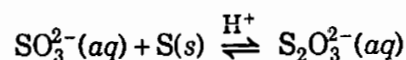
The two labelled chlorine would rapidly exchange with three non-labelled ones, if all five chlorines are in a similar environment, and as a result all five chlorines would have radioactive character. If above synthesised  $\text{PCl}_5$  is hydrolysed.



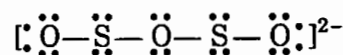
HCl is found to be radioactive and  $\text{POCl}_3$  is found to be non-radioactive. Thus, two chlorines are different from the other three.

- To decide structure of  $\text{S}_2\text{O}_3^{2-}$ .

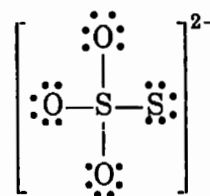
The formula of thiosulphate ion is  $\text{S}_2\text{O}_3^{2-}$ . Following reaction is found to be reversible depending on the experimental conditions :



If one starts with elemental sulphur enriched with the radioactive sulphur-35, the isotope acts as a "label" for S atoms. All the labels are found in the sulphur precipitated when  $\text{S}_2\text{O}_3^{2-}(\text{aq})$  is treated with dilute acids. Thus, two sulphur atoms are not structurally equivalent as would be case if the structure were:

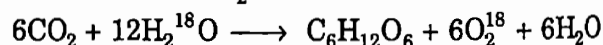


Otherwise, the radioisotope would be present in both the sulphur atoms. Based on this thiosulphate has the structure:



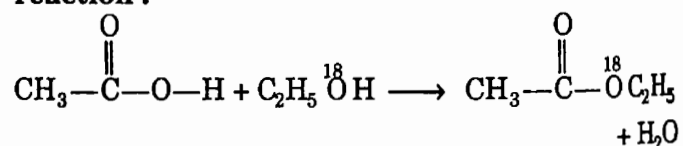
Oxidation number of central S atom is +6 and that of terminal is -2, thus net oxidation number is 4 (for two S-atoms) and difference is 8.

Study of photosynthesis also uses radioisotope  $^{18}\text{O}$  to determine the source of  $\text{O}_2$



On starting with  $^{18}\text{O}$  enriched water ( $\text{H}_2^{18}\text{O}$ ) we find that only  $\text{O}_2$  has radioisotope indicating that  $\text{O}_2$  comes only from  $\text{H}_2\text{O}$  and not from  $\text{CO}_2$ .

- To study the mechanism of the following reaction :



O of  $\text{C}_2\text{H}_5\text{OH}$  is enriched with radioisotope  $^{18}\text{O}$ . After esterification,  $^{18}\text{O}$  is found in the ester and not in  $\text{H}_2\text{O}$  indicating  $-\text{OH}$  of  $\text{CH}_3\text{COOH}$  is replaced by  $-\text{OC}_2\text{H}_5$  of  $\text{C}_2\text{H}_5\text{OH}$  which acts as an acid in this reaction.

**Illustration 1** What is the age of a bone fragment that shows an average of 2.9 disintegrations per minute (dpm) per gram of carbon? The carbon in living organisms undergoes an average of 15.3 dpm/min per gram, and the half-life of  $^{14}\text{C}$  is 5715 years.

**Solution**  $T_{50}$  of  $^{14}\text{C}$  = 5715 yr

$$\therefore \text{decay constant } \lambda = \frac{0.693}{T_{50}} = \frac{0.693}{5715 \text{ yr}}$$

$$= 1.2126 \times 10^{-4} \text{ yr}^{-1}$$

Also, 
$$\lambda = \frac{2.303}{t (\text{age})} \log \frac{N_0}{N}$$

where  $N_0$  the initial activity = 15.3 dpm and  $N$  the activity after time  $t = 2.9$  dpm

$$\therefore 1.2126 \times 10^{-4} = \frac{2.303}{t} \log \frac{15.3}{2.9}$$

$$t = 13718 \text{ yr}$$

**Illustration 2** A 1.00 mL solution containing 0.240  $\mu\text{Ci}$  of tritium is injected into a dog's bloodstream. After a period of time to allow the isotope to be dispersed, a 1.00 mL sample of blood is drawn. The radioactivity of this sample is found to be  $4.3 \times 10^{-4} \mu\text{Ci/mL}$ . What is the total volume of blood in the dog?

**Solution** Let total volume =  $X$  mL

$$\text{Activity} = 0.240 \mu\text{Ci}$$

$$\text{Activity per mL} = 0.240 \mu\text{Ci}/X$$

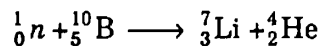
After dilution in the blood stream

$$\text{activity per mL} = 4.3 \times 10^{-4} \mu\text{Ci/mL}$$

Thus, 
$$0.240 \mu\text{Ci}/X = 4.3 \times 10^{-4} \mu\text{Ci/mL}$$

$$\therefore X = 558.14 \text{ mL}$$

Alpha and beta-particles can be detected by a Geiger counter. To detect neutrons, boron trifluoride is added to the gas in the tube. Neutrons react with boron-10 nuclei to produce alpha particles, which can then be detected.



A **scintillation counter** is a device that detects nuclear radiations from flashes of light generated in a material by the radiation. A phosphor is a substance that emits flashes of light when struck by radiation. The gamma rays are detected by this counter— a sodium iodide crystal containing thallium (I) iodide is used as a phosphor for gamma radiations. Rutherford used zinc sulphide as a phosphor to detect alpha particles.

## Biological Effects and Radiation Dosage

Quantity of radiation intermixing with biological organisms might be small but the effects are quite adverse because important chemical bonds may be broken; DNA is specially affected.

Effect of nuclear radiations on biological tissues is expressed in terms of RAD (radiation adsorbed dose) which is the dosage of radiation that deposits  $1 \times 10^{-2} \text{ J}$  of energy per kilogram of tissue.

- Neutrons are more destructive than gamma rays of the same radiation dosage measured in rads.

A REM (roentgen equivalent for man) is a unit of radiation dosage used to relate various kinds of radiation in terms of biological destruction.

$$\text{Rem} = \text{rad} \times \text{RBE}$$

where RBE stands for the **relative biological effectiveness**.

- For beta and gamma-radiations,  $\text{RBE} \approx 1$  radiation.
- For neutron,  $\text{RBE} \approx 5$
- For alpha-radiation,  $\text{RBE} \approx 10$ .

The biological effects of different radiation-doses are given in Table 5.8

**Table 5.8 Biological Effects of Short-Term Radiation on Humans**

| Dose (rem) | Biological effect                                                 |
|------------|-------------------------------------------------------------------|
| 0–25       | No detectable effects                                             |
| 25–100     | Temporary decrease in white blood cell count                      |
| 100–200    | Nausea, vomiting, longer-term decrease in white blood cells       |
| 200–300    | Vomiting, diarrhoea, losses of appetite, restlessness             |
| 300–600    | Vomiting, diarrhoea, hemorrhaging, eventually death in some cases |
| above 600  | Eventually death in nearly all cases.                             |

## Radiations and Matter

### Detection and Biological Effects

Radiations from nuclear processes affect matter in part by dissipating energy in it. In some cases, these radiations may also excite electrons in matter. When these electrons undergo transitions back to their ground states, light is emitted. The ions, free electrons and light produced in matter can be used to detect nuclear radiations. Because nuclear radiations can ionise molecules and break chemical bonds, they adversely affect biological organisms.

### Radiation Counters

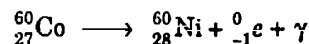
A **Geiger counter**, a kind of ionisation counter used to count particles emitted by radioactive nuclei consists of a metal tube fitted with gas such as argon.

## Target Practice 2

1. What is Einstein mass-energy relationship? .....
2. When an electron is emitted, mass number remains unchanged but atomic number increases by one unit. Write nuclear reaction. ....
3. Write full name of MRI.
4. What is application of radioactive sodium chloride containing sodium-24?

5. Which radioactive isotope is used to control polycythemia vera?

6. Cobalt-60 is used to irradiate tumors with  $\gamma$ -rays.



Which is responsible for destroying cancer-cells?

7. A museum wishes to analyse a piece of ruby for chromium content. What should be preferred method of analysis?

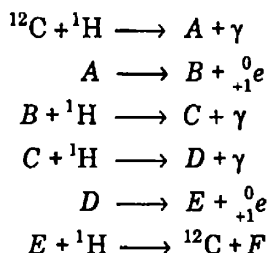
### Answers

1.  $E = mc^2$
2.  ${}^1_0n \longrightarrow {}^1_1\text{H} + {}^0_{-1}e$
3. Magnetic Resonance Imaging
4. It is used to study obstructive vascular diseases in the extremities of the body.

5. Phosphorus-32
6.  $\gamma$ -rays,
7. Neutron activation analysis.

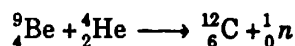
## Practice Exercise 2

1. The half-life periods of two elements A and B are 5 days and 5 months, respectively. Which of the two is more stable?
2. Which of the following are not stable?
  - (i)  ${}^{14}_6\text{C}$
  - (ii)  ${}^{13}_6\text{C}$
  - (iii)  ${}^{14}_7\text{N}$
  - (iv)  ${}^{24}_{11}\text{Na}$
3. A proposed series of reactions (known as the carbon-nitrogen cycle) that could be important in every hottest region of the interior of the sun is:



Identify the series labelled A to F.

4. Give product of the following nuclear reactions:
  - (a)  ${}^{109}_{47}\text{Ag} + {}^4_2\text{He} \longrightarrow ?$
  - (b)  ${}^{10}_5\text{B} + {}^4_2\text{He} \longrightarrow ? + {}^1_0n$
  - (c)  ${}^{246}_{96}\text{Cm} + {}^{12}_6\text{C} \longrightarrow ? + 4{}^1_0n$
  - (d)  ${}^{250}_{98}\text{Cf} + {}^{11}_5\text{B} \longrightarrow ? + 4{}^1_0n$
5. Write balanced nuclear equations for the following processes:
  - (a) Alpha emission of  ${}^{162}\text{Re}$
  - (b) Electron capture of  ${}^{138}\text{Sm}$
  - (c) Beta emission of  ${}^{188}\text{W}$
  - (d) Positron emission of  ${}^{165}\text{Ta}$
6. Write the abbreviated notation for the following bombardment reaction, in which neutron was first discovered:

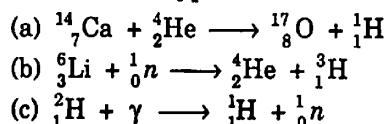


7. Write the nuclear equation for the bombardment reaction denoted as  ${}^{27}_{13}\text{Al} (p, d) {}^{26}_{13}\text{Al}$ .

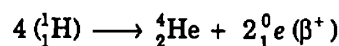
8. Complete the following nuclear reactions:



9. What are the types of reactions?



10. How a radioactive nucleus can emit a  $\beta^-$  particle (electron) if there are no electrons present in the nucleus?
11. Why both  $\alpha$  and  $\beta$ -particles are emitted in a radioactive decay series?
12. Why is  ${}^{238}_{92}\text{U}$  not suitable for a chain reaction?
13. A typical neutron-initiated fission of  ${}^{235}_{92}\text{U}$  yields  ${}^{97}_{42}\text{Mo}$ , two neutrons and an isotope of what element?
14. If an atom of  ${}^{235}_{92}\text{U}$ , after the absorption of a slow neutron undergoes fission to form two fragments  ${}^{139}_{54}\text{Xe}$  and  ${}^{94}_{38}\text{Sr}$ , what other particles are produced and how many?
15. The binding energy per nucleon for  ${}^{235}_{92}\text{U}$  is 7.5 MeV and 8.5 MeV for nuclei of half that mass. If  ${}^{235}_{92}\text{U}$  undergoes nuclear fission in two such nuclei of equal size, how much energy is released in the process?
16. The overall reaction in the sun responsible for the energy it radiates is



It has been estimated that the sun produces  $3 \times 10^{22} \text{ kJ s}^{-1}$ . How many moles of H-atoms are converted to He in 1 second, to produce this energy? (Take binding energy 27 MeV)

17. Fill in the blanks:
  - (a) ..... is a thermonuclear reaction.

- (b) The energy production in the sun and stars could be explained on the basis of ..... by means of which hydrogen is converted into helium.
- (c) ..... was awarded the 1967 Physics Nobel Prize for his theory of energy production in the sun and the stars.
- (d) Hydrogen bomb is based on .....
- (e) Instrument used to accelerate nuclear projectiles is called .....
- (f) ..... was awarded the 1939 Physics Nobel Prize for invention and development of cyclotron.
- (g)  ${}^9_4\text{Be} + {}^4_2\text{He} \longrightarrow {}^{12}_6\text{C}$  led to the discovery of ..... by Chadwick.
18. Make distinction between nuclear fusion and nuclear fission.
19. An artificial element shows activity of 12.5 cps (counts per second) at its formation as recorded in a G.M. counter. After 10 min activity is 7.5 cps. In the absence of element, G.M. counter records activity of 2.5 cps. What is its half-life period and activity after 20 days?
20. Give one example each of (i)  $\alpha$ -particle-induced reaction (ii) proton-induced reaction and (iii) neutron-induced reaction.
21. Packing fraction of element A, B, C are -20, 27, +18, respectively. Arrange them in the increasing order of stability.

### Answers

- Element B is more stable.
- (i)  ${}^{14}_6\text{C}$  (ii)  ${}^{13}_6\text{C}$  and (iv)  ${}^{24}_{11}\text{Na}$  are not stable.
- A:  ${}^{13}_7\text{N}$  B:  ${}^{13}_6\text{C}$  C:  ${}^{14}_7\text{N}$  D:  ${}^{16}_8\text{O}$  E:  ${}^{15}_7\text{N}$   
F:  ${}^4_2\text{He}$
- (a)  ${}^{113}_{49}\text{In}$  (b)  ${}^{13}_7\text{N}$  (c)  ${}^{264}_{102}\text{No}$  (d)  ${}^{257}_{103}\text{Lr}$
- (a)  ${}^{162}_{75}\text{Re} \longrightarrow {}^{158}_{73}\text{Ta} + {}^4_2\text{He}$   
(b)  ${}^{138}_{62}\text{Sm} + {}^0_{-1}e \longrightarrow {}^{138}_{61}\text{Pm}$   
(c)  ${}^{188}_{74}\text{W} \longrightarrow {}^{188}_{76}\text{Re} + {}^0_{-1}e$   
(d)  ${}^{163}_{73}\text{Ta} \longrightarrow {}^{165}_{72}\text{Hf} + {}^0_{-1}e$
- ${}^9_4\text{Be} (\alpha, n) {}^{12}_6\text{C}$  7.  ${}^{27}_{13}\text{Al} + {}^1_1\text{H} \longrightarrow {}^{26}_{13}\text{Al} + {}^2_1\text{H}$
- (i)  ${}^{40}_{20}\text{Ca} + {}^1_0n \longrightarrow {}^{37}_{18}\text{Ar} + {}^4_2\text{He}$   
(ii)  ${}^{24}_{12}\text{Mg} + {}^2_1\text{H} \longrightarrow {}^{22}_{11}\text{Na} + {}^4_2\text{He}$   
(iii)  ${}^3_1\text{H} + {}^4_2\text{He} \longrightarrow {}^6_3\text{Li} + {}^1_0n$   
(iv)  ${}^{197}_{79}\text{Au} + {}^1_0n \longrightarrow {}^{198}_{79}\text{Au} + \gamma$
- (v)  ${}^{27}_{13}\text{Al} + \gamma \longrightarrow {}^{26}_{13}\text{Al} + {}^1_0n$   
(vi)  ${}^9_4\text{Be} + {}^4_2\text{He} \longrightarrow {}^{12}_6\text{C} + {}^1_0n$
- (a)  $\alpha, p$ ; (b)  $n, \alpha$ ; (c)  $\gamma, n$ . 10. See text
- See text 12. Due to less stability 13.  ${}^{137}_{50}\text{Sn}$
- Three neutrons 15. 235 MeV
- $4.61 \times 10^{13}$  mol H atoms  $\text{s}^{-1}$ .
- (a) nuclear fusion (b) carbon-cycle (c) H.A. Bethe  
(d) nuclear fusion (e) cyclotron (f) E.O. Lawrence  
(g) neutron
- See Text
- half-life = 10 days, 5 cps (2.5 cps is zero error of the G.M. counter.)
- ${}^{14}_7\text{N} (\alpha, n) {}^{17}_9\text{F} \longrightarrow {}^{17}_8\text{O} + {}^0_{+1}e$   
 ${}^{11}_5\text{B} (p, n) {}^{11}_6\text{C} \longrightarrow {}^{11}_5\text{B} + {}^0_{+1}e$   
 ${}^{23}_{11}\text{Na} (n, \gamma) {}^{24}_{11}\text{Na} \longrightarrow {}^{24}_{12}\text{Mg} + {}^0_{-1}e$
- $C < A < B$ .

# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** Calculate the nuclear binding energy per nucleon of  $^{12}_6\text{C}$  from the following data:

Given mass of proton ( $m_p$ ) = 1.00758 amu

mass of neutron ( $m_n$ ) = 1.00893 amu

mass of electron ( $m_e$ ) = 0.00055 amu

Isotopic mass of  $^{12}\text{C}$  = 12.00000 amu. Take

1 amu = 931 MeV

**Plan** From the mass defect  $\Delta m$  (amu),

$$\text{binding energy} = \Delta m \times 931 \text{ MeV}$$

$$\text{binding energy per nucleon} = \frac{\Delta m \times 931}{\text{number of nucleons}}$$

**Solution**  $^{12}_6\text{C}$  contains 6 protons, 6 neutrons and 6 electrons hence, calculated atomic mass of  $^{12}_6\text{C}$

$$= 6m_p + 6m_n + 6m_e$$

$$= 6 \times 1.00758 + 6 \times 1.00893 + 6 \times 0.00055$$

$$= 12.10236$$

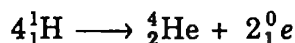
$$\therefore \text{mass defect} = 12.10236 - 12.00000$$

$$= 0.10236 \text{ amu}$$

$$\text{binding energy} = 0.10236 \times 931 = 95.30 \text{ MeV}$$

$$\text{binding energy per nucleon} = \frac{95.30}{12} = 7.94 \text{ MeV}$$

**Problem 2.** The sun radiates energy at the rate of  $4 \times 10^{26} \text{ J s}^{-1}$ . If the energy of fusion process



is 27 MeV, calculate amount of hydrogen that would be consumed per day for the given process.

**Plan** Energy radiated by the sun per second is to be converted per day. Energy of the fusion process is known, hence, amount of  $^1_1\text{H}$  can be calculated.

$$\text{Solution } 27 \text{ MeV} = 27 \times 10^6 \times 1.6 \times 10^{-19} \text{ J}$$

$$= 43.2 \times 10^{-13} \text{ J}$$

$$\text{and } 4 \times 10^{26} \text{ J s}^{-1} = 4 \times 10^{26} \times 24 \times 3600 \text{ J day}^{-1}$$

$$= 34.56 \times 10^{30} \text{ J day}^{-1}$$

$43.2 \times 10^{-13} \text{ J}$  of energy is obtained from

$$= 4 \text{ amu of H}$$

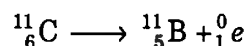
$$= \frac{4}{6.02 \times 10^{23}} \text{ g of H}$$

$34.56 \times 10^{30} \text{ J day}^{-1}$  of energy is obtained from

$$= \frac{4}{6.02 \times 10^{23}} \times \frac{34.56 \times 10^{30}}{43.2 \times 10^{-13}} \text{ g H}$$

$$= 53.16 \times 10^{18} \text{ g}$$

**Problem 3.** A chemist prepares 1.00 g of pure  $^{11}_6\text{C}$ . This isotope has half-life of 21 min, decaying by equation :



(a) What is rate of disintegration per second (dps) at start?

(b) How much of this isotope ( $^{11}_6\text{C}$ ) is left after 24 h of its preparation?

**Plan**  $-\frac{dN}{dt} = \lambda N_0$ , where  $N_0$  is the number of atoms of  $^{11}_6\text{C}$  at start in 1 g.

$$\text{Use } \lambda = \frac{2.303}{t} \log \frac{N_0}{N}$$

$$\text{or } C = C_0 \left(\frac{1}{2}\right)^y \text{ to calculate amount left after 24 h}$$

$$\text{Solution (a) } -\frac{dN}{dt} = \lambda N_0$$

$$\text{where } \lambda \text{ (disintegration constant)} = \frac{0.693}{T_{50}} \text{ and } N_0 \text{ the}$$

number of atoms present initially

$$N_0 = \frac{\text{weight}}{\text{atomic weight}} \times \text{Avogadro's number}$$

$$-\frac{dN}{dt} = \frac{0.693}{21 \times 60} \times \frac{1}{11} \times 6.02 \times 10^{23} \text{ dps}$$

$$= 3 \times 10^{19} \text{ dps}$$

$$\text{(b) Using equation : } C = C_0 \left(\frac{1}{2}\right)^y$$

$$\text{where, } y = \frac{\text{total time}}{T_{50}} = \frac{24 \times 60 \text{ min}}{21 \text{ min}} = 68.57$$

$$C_0 = \text{initial amount} = 1 \text{ g}$$

$$C = \text{amount of radioactive substance left after } y \text{ half-lives}$$

$$\therefore C = 1 \left(\frac{1}{2}\right)^{68.57}$$

$$\text{Taking log and then antilog, } C = 2.28 \times 10^{-21} \text{ g } (^{11}_6\text{C}).$$

**Problem 4.** Calculate the weight in grams of 1 Ci of  $^{14}\text{C}$  ( $T_{50} = 5000$  yr), ( $1 \text{ yr} = 31.536 \times 10^6 \text{ s}$ ).

*Plan* 
$$-\frac{dN}{dt} = \lambda N = \lambda \frac{w}{A} N_0$$

where  $w$  is the weight of the element of mass number  $A$ ;  $N_0$  is the Avogadro's number.

**Solution** Let weight required =  $w \text{ g}$

$$= \frac{w}{14} \times 6.02 \times 10^{23} \text{ atoms}$$

Disintegration constant ( $\lambda$ ) =  $\frac{0.693}{5000 \times 31.536 \times 10^6 \text{ s}^{-1}}$

and  $1 \text{ Ci} = 3.7 \times 10^{10} \text{ dps}$

$$-\frac{dN}{dt} = \lambda N$$

$$3.7 \times 10^{10} = \frac{0.693 \times w \times 6.02 \times 10^{23}}{5000 \times 31.536 \times 10^6 \times 14}$$

$$w = 0.196 \text{ g}$$

**Problem 5.** How many mL of radon (Rn) under standard condition of temperature and pressure are in equilibrium with 1 g of radium (Ra). Given half-life period of  $^{226}\text{Ra} = 1590$  yr and for  $^{222}\text{Rn} = 3.82$  days.

*Plan* At radioactive equilibrium :

$$N_1 \lambda_1 = N_2 \lambda_2 \quad \therefore \frac{N_1}{N_2} = \frac{\lambda_2}{\lambda_1}$$

**Solution**

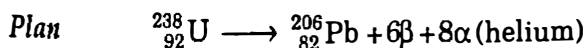
$$\frac{N_1(\text{Rn})}{N_2(\text{Ra})} = \frac{\lambda_2(\text{Ra})}{\lambda_1(\text{Rn})} = \frac{T_{50}(\text{Rn})}{T_{50}(\text{Ra})}$$

$$\frac{N_1(\text{Rn})}{(1/226) \text{ mol}} = \frac{3.82 \text{ days}}{365 \times 1590 \text{ days}}$$

$$N_1(\text{Rn}) = 2.91 \times 10^{-8} \text{ mol}$$

$\therefore$  mL of Rn at STP =  $6.52 \times 10^{-4} \text{ mL}$

**Problem 6.** Estimate the age of a rock which is found to contain  $5 \times 10^{-5} \text{ mL}$  of helium at STP and  $3 \times 10^{-7} \text{ g}$  of uranium. ( $T_{50}$  of  $^{238}_{92}\text{U}$  is  $4.51 \times 10^9$  yr and each  $^{238}_{92}\text{U}$  is converted into  $^{206}_{82}\text{Pb}$ ).



We take the equation  $\left[ \frac{[\text{Pb}]}{[\text{U}]} + 1 \right] = (2)^y$

where  $\frac{[\text{Pb}]}{[\text{U}]}$  is the molar ratio,  $y = \frac{t}{T_{50}}$

**Solution** Number of moles of He at STP

$$= \frac{5 \times 10^{-5}}{22400} \text{ mol}$$

$$[\text{Pb}] = \frac{1}{8} [\text{He}] = \frac{5 \times 10^{-5}}{8 \times 22400} \text{ mol}$$

$$= 2.79 \times 10^{-10} \text{ mol}$$

$$[\text{U}] = \frac{3 \times 10^{-7}}{238} = 12.6 \times 10^{-10} \text{ mol}$$

$$\therefore \left[ \frac{2.79 \times 10^{-10}}{12.6 \times 10^{-10}} + 1 \right] = (2)^y$$

$$1.2214 = (2)^y$$

taking log, we have  $y = 0.2886$

but  $y = \text{total number of half-life} = \frac{t}{T_{50}}$

$$\begin{aligned} \therefore t &= y \times T_{50} \\ &= 0.2886 \times 4.5 \times 10^9 \\ &= 1.30 \times 10^9 \text{ yr} \end{aligned}$$

**Problem 7.** 1 g of radium produces  $0.043 \text{ cm}^3$  of helium gas at STP in one year. The number of  $\alpha$ -particles produced in the same period is  $11.6 \times 10^{17}$ . Calculate the value of Avogadro's number.

*Plan* One mole =  $22400 \text{ cm}^3$  at STP =  $N_0$

Thus, from the volume of the gas and number of particles,  $N_0$  can be determined.



thus,  $0.043 \text{ cm}^3$  of helium gas at STP

$$= 11.6 \times 10^{17} \alpha\text{-particles}$$

$$\therefore 22400 \text{ cm}^3 \text{ of helium at STP} = \frac{11.6 \times 10^{17}}{0.043} \times 22400$$

$$N_0 = 6.043 \times 10^{23} \text{ mol}^{-1}$$

**Problem 8.** The curie was originally intended to be the activity of one gram of radium-226, [ $T_{50} = 1620 \text{ a}$ , here 'a' stands for annum (year) in SI unit]. Calculate actual weight of radium which is equivalent to one curie. given  $1 \text{ a} = 3.1536 \times 10^7 \text{ s}$

*Plan* 
$$-\frac{dN}{dt} = -\lambda N = -\lambda \frac{w}{A} N_0$$

Thus,  $w$  (mass of the radioactive substance) can be calculated.

**Solution** 
$$\lambda = \frac{0.693}{1620} = \frac{0.693}{1620 \times 3.1536 \times 10^7 \text{ s}^{-1}}$$

but by definition, 1 Ci (curie) =  $3.7 \times 10^{10} \text{ dps}$

$$\therefore -\frac{dN}{dt} = \lambda N$$

$$3.7 \times 10^{10} = \frac{0.693}{1620 \times 3.1536 \times 10^7} N$$

$$\therefore N = 2.72766 \times 10^{21} \text{ atoms}$$

$$\text{moles of Ra-226} = \frac{2.72766 \times 10^{21}}{6.02 \times 10^{23}}$$

$$= 0.004531$$

$$\text{amount in g} = \text{mol} \times 226$$

$$= 1.024 \text{ g}$$

**Problem 9.** The half-life of  $^{32}\text{P}$  is 14.3 days. Calculate the specific activity of a specimen of phosphorus containing 1.00 part per million  $^{32}\text{P}$ . (atomic wt. of P = 31)

**Plan** Determine rate of disintegration per second (dps) for the given isotope. Activity of 1 curie =  $3.7 \times 10^{10}$  dps. Thus, activity in the given isotope can be calculated.

**Solution** The specific activity of a radionuclide is its activity per kg of the radioactive material.

$$1 \text{ kg} = 1000 \text{ g } ^{31}\text{P} = \frac{1000}{31} N_0 \text{ atoms of } ^{31}\text{P}$$

But  $^{32}\text{P}$  content is 1 ppm (1 atm  $^{32}\text{P}$  out of  $10^6$  atoms)

$$\therefore ^{32}\text{P} = \frac{1000 N_0}{31} \times \frac{1}{10^6} = \frac{1000 \times 6.02 \times 10^{23}}{31 \times 10^6}$$

$$= 1.942 \times 10^{19} \text{ atoms of } ^{32}\text{P}$$

$$\text{also } -\frac{dN}{dt} = \lambda N, \quad \left( \lambda = \frac{0.693}{T_{50}} \right)$$

$$-\frac{dN}{dt} = \frac{0.693}{14.3 \times 24 \times 3600} \times 1.942 \times 10^{19} \text{ dps}$$

$$= 1.089 \times 10^{13} \text{ s}^{-1}.$$

hence, specific activity (number of curies in 1 kg of  $^{32}\text{P}$ )

$$= \frac{1.089 \times 10^{13}}{3.7 \times 10^{10}} = 294.32 \text{ Ci kg}^{-1}$$

**Problem 10.** An archaeological specimen containing  $^{14}\text{C}$  gives 40 counts in 5 min per gram of carbon. A specimen of freshly cut wood gives 20.3 counts per gram of carbon per minute. The counter used recorded a background count of 5 counts per minute in absence of any  $^{14}\text{C}$ -containing sample. What is the age of the specimen? [ $T_{50}$  of  $^{14}\text{C}$  = 5668 a]

**Plan** Initial and final activities (in terms of counts per min) have been given. Net value are determined (since instruments has zero-error). Thus, age can be determined.

**Solution** Counter has zero-error of 5 counts per min (cpm)

$$\therefore \text{Initial activity} = 20.3 - 5 = 15.3 \text{ cpm}$$

$$\text{Activity after time } t = \left( \frac{40}{5} - 5 \right) = 3.0 \text{ cpm}$$

$$\therefore \lambda = \frac{2.303}{t} \log \frac{15.3}{3.0}$$

$$\frac{0.693}{5668} = \frac{2.303}{t} \log \frac{15.3}{3.0}$$

$$\therefore t = 13328 \text{ yr}$$

**Problem 11.** Calculate the energy released in the reaction :



[(Cl-35) = 34.9688 amu, (S-35) = 34.9690 amu, (H-1) = 1.0078 amu,  ${}^1_0n$  = 1.0087 amu] Assume 1 amu = 931 MeV

**Plan** From the mass defect ( $\Delta m$ )

$$\text{energy (in MeV)} = (\Delta m \text{ in amu} \times 931)$$

**Solution** Mass defect

$$\Delta m = [m(\text{Cl}) + m(n)] - [m(\text{S}) + m(\text{H})]$$

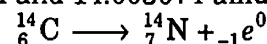
$$= [34.9688 + 1.0087] - [34.9690 + 1.0078]$$

$$= 0.0007 \text{ amu}$$

$$\therefore \text{energy released} = 0.0007 \times 931$$

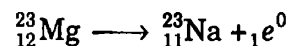
$$= 0.6517 \text{ MeV}$$

**Problem 12.** Calculate the maximum energy of a  $\beta$ -particle emitted from a  $^{14}\text{C}$  nucleus which does not emit any  $\gamma$ -radiation. The masses of C-14 and N-14 isotopes are 14.003242 amu and 14.003074 amu respectively.



**Plan** In solving the above problem, the mass of emitted  $\beta$ -particle is not taken into account. This is because the atom N-14 produced contains one more extra nuclear electron than the C-14 atom. But when a positron is emitted two electron masses have to be taken into account

- one for the positron emitted and
- one for the extra electron that has to leave the extra nuclear shells to maintain electrical neutrality. Thus in the reaction :



$$\Delta m = [\text{mass of (Mg - 23)}] - [\text{mass of (Na - 23)} + 2 \text{ mass of electron}]$$

**Solution**  $\Delta m = m(\text{C-14}) - m(\text{N-14}) = 0.000168 \text{ amu}$

$$\therefore \text{energy released in the process} = 0.000168 \times 931$$

$$= 0.1564 \text{ MeV}$$

This is maximum energy of  $\beta$ -particle.

**Problem 13.** A sample of  $^{90}_{38}\text{Sr}$  originally had an activity of 0.500 mCi (millicurie) (a) What is the specific activity of the sample? (b) What is the activity of the sample after 30.0 years?  $T_{30}$  of  $^{90}_{38}\text{Sr}$  is 19.9 years.

**Plan** Initial activity ( $N_0$ ) is known, hence activity ( $N$ ) after time  $t$  can be calculated using

$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N}$$

**Solution** The specific activity of a radio-nuclide is its activity per kg of the radioactive material. Hence, first we calculate the weight of  $^{90}_{38}\text{Sr}$  which has an activity of 0.500 mCi

$$\therefore -\frac{dN}{dt} = \lambda N = \lambda \frac{wN_0}{A}$$

$$1 \text{ mCi} = 3.7 \times 10^7 \text{ dps}$$

$$\therefore 0.500 \text{ mCi} = 0.5 \times 3.7 \times 10^7 \text{ dps}$$

$$0.5 \times 3.7 \times 10^7 = \frac{0.693 \times w \times 6.02 \times 10^{23}}{19.9 \times 365 \times 24 \times 60 \times 60 \times 90}$$

$$w = 2.5 \times 10^{-6} \text{ g} = 2.5 \times 10^{-9} \text{ kg}$$

$$\text{Specific activity} = \frac{0.5 \times 3.7 \times 10^7}{2.5 \times 10^{-9}}$$

$$= 7.4 \times 10^{15} \text{ dis/kg-s}$$

$$(b) \text{ using } N = N_0 \left(\frac{1}{2}\right)^y$$

$$\text{where } y = \frac{t}{T_{50}} = \frac{30.0}{19.9} = 1.5075$$

$$N = 0.5 \left(\frac{1}{2}\right)^{1.5075} \text{ mCi}$$

$$\begin{aligned} \text{taking log } \log N &= \log 0.5 - 1.5075 \log 2 \\ &= -0.3010 - 1.5075 \times 0.3010 \\ &= -0.7548 \end{aligned}$$

$$\begin{aligned} N &= 0.176 \text{ mCi} \\ &= 0.176 \times 3.7 \times 10^7 \text{ dps} \\ &= 6.51 \times 10^6 \text{ dps} \end{aligned}$$

**Problem 14.** In order to determine the volume of blood in an animal without killing it, a 1.00 mL sample of an aqueous solution containing tritium is injected into the animal's blood-stream. The sample injected has an activity of  $1.8 \times 10^6$  cps (counts per second). After sufficient time for the sample to be completely mixed with the animal's blood due to normal blood circulation, 2.00 mL of blood are withdrawn from animal, and the activity of the blood sample withdrawn is found to be  $1.2 \times 10^4$  cps. Calculate volume of animal's blood.

*Plan* Compare the activity with volume of the blood sample to calculate volume of animal blood.

**Solution** Let volume of the blood in the animal =  $V$  mL

$$\text{Total activity before mixing} = 1.8 \times 10^6 \text{ cps}$$

$$\begin{aligned} \text{Total activity after mixing in } V \text{ mL} &= \frac{1.2 \times 10^4}{2} \times V \\ &= 0.6 \times 10^4 V \text{ cps} \end{aligned}$$

$$\begin{aligned} \text{Thus, } 0.6 \times 10^4 V &= 1.8 \times 10^6 \\ (\text{assuming activity remains constant}) \\ V &= \frac{1.8 \times 10^6}{0.6 \times 10^4} = 300 \text{ mL} \end{aligned}$$

**Problem 15.** A sample of uraninite, a uranium containing mineral, was found on analysis to contain 0.214 g of lead-206 for every g uranium. If all the lead came from the radioactive disintegration of the uranium and assume that all isotopes of uranium other than  $^{238}\text{U}$  can be neglected, estimate the date when the mineral was

formed in the earth's crust? (The half-life of  $^{238}\text{U}$  is  $4.5 \times 10^9$  years).

$$\text{Plan Use } 1 + \frac{[\text{Pb}]}{[\text{U}]} = 2^y \text{ where } y = \frac{t}{T_{50}}.$$

**Solution** If 0.214 g of  $^{206}\text{Pb}$  is present, then 1 g of  $^{238}\text{U}$  is also present.

$$\therefore [\text{Pb}] = \frac{0.214}{206} = 0.00104 \text{ mol}, [\text{U}] = \frac{1}{238} = 0.0042 \text{ mol}$$

$$\therefore \frac{[\text{Pb}]}{[\text{U}]} = 0.247$$

$\therefore$  For 'rock dating' analysis, we use

$$\left[1 + \frac{[\text{Pb}]}{[\text{U}]}\right] = 2^y \text{ where } y = \frac{t}{T_{50}}$$

$$[1 + 0.247] = (2)^y$$

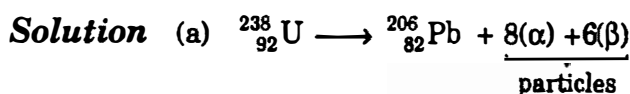
Taking log, we get  $y = 0.3188$

$$\therefore \frac{t}{T_{50}} = 0.3188$$

$$\begin{aligned} \therefore t &= 0.3188 \times T_{50} \\ &= 0.3188 \times 4.5 \times 10^9 \\ &= 1.4344 \times 10^9 \text{ years} \end{aligned}$$

**Problem 16.** Given 2.00 kg of  $^{238}_{92}\text{U}$  ( $T_{50} = 4.50 \times 10^9$  years). The ultimate decay product in this series is  $^{206}_{82}\text{Pb}$ . (a) What weight of  $^{238}_{92}\text{U}$  is left after  $3.00 \times 10^9$  years? (b) What weight of  $^{206}_{82}\text{Pb}$  is produced in this time?

*Plan* Use  $C = C_0 \left(\frac{1}{2}\right)^y$  where  $C_0$  is the initial amount,  $C$  after time  $t$  and  $y = \frac{t}{T_{50}}$ .



$$\text{taking } C = C_0 \left(\frac{1}{2}\right)^y \text{ where } y = \frac{3.00 \times 10^9}{4.5 \times 10^9} = 0.667$$

$$C = 2 \left(\frac{1}{2}\right)^{0.667}$$

taking log on both sides

$$\begin{aligned} \text{or } \log C &= \log 2 - 0.667 \log 2 \\ &= 0.3010 - 0.666 \times 0.3010 = 0.1003 \end{aligned}$$

$$\therefore C = 1.26 \text{ kg}$$

$$\begin{aligned} \therefore (b) \text{ } ^{92}\text{U disintegrated} &= 2.00 - 1.26 \\ &= 0.74 \text{ kg} = 740 \text{ g} \\ &= \frac{740}{238} = 3.109 \text{ mol} \end{aligned}$$



$$\begin{aligned}\therefore \text{Pb formed} &= 3.109 \text{ mol} \\ &= 3.109 \times 206 = 640.5 \text{ g} \\ &= 0.6405 \text{ kg}\end{aligned}$$

**Problem 17.** A sample of  $^{14}\text{CO}_2$  was to be mixed with ordinary  $\text{CO}_2$  for a biological tracer experiment. In order that  $10 \text{ cm}^3$  of the diluted gas at STP should have  $10^4$  dis/min, how many  $\mu\text{Ci}$  of radioactive carbon-14 are needed to prepare  $0.06 \text{ m}^3$  of the diluted gas?

**Plan** Given volume is to be related to the dps (activity) and thus, number of microcuries ( $\mu\text{Ci}$ ) can be calculated.

**Solution**  $10 \text{ cm}^3$  of the diluted gas has activity

$$= 10^4 \text{ dis/min} = \frac{10^4}{60} \text{ dps}$$

$$\therefore 0.06 \text{ m}^3 (= 60,000 \text{ cm}^3) \text{ of the diluted gas has}$$

$$\text{activity} = \frac{10^4}{60} \times \frac{60000}{10} \text{ dps}$$

$$\begin{aligned}\text{hence, number of } \mu\text{Ci needed} &= 10^4 \times \frac{60000}{600 \times 3.7 \times 10^4} \\ &= 27.03 \mu\text{Ci}\end{aligned}$$

**Problem 18.** The half-life of  $^{212}\text{Pb}$  is 10.6 h, that of its daughter  $^{212}\text{Bi}$  is 60.5 min. How long will it take for a maximum daughter activity to grow in freshly separated  $^{212}\text{Pb}$ ?

**Plan** We define time of maximum activity by equation

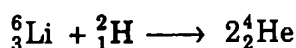
$$t_{\max} = \frac{2.303}{(\lambda_d - \lambda_p)} \log \frac{\lambda_d}{\lambda_p}$$

where  $\lambda_d$  is the disintegration constant of daughter element and  $\lambda_p$  that of parent element.

$$\begin{aligned}\text{Solution } \lambda_d &= \frac{0.693}{T_{50} (^{212}\text{Bi})} = \frac{0.693}{60.5 \text{ min}} \\ &= 0.01145 \text{ min}^{-1} \\ \lambda_p &= \frac{0.693}{T_{50} (^{212}\text{Pb})} = \frac{0.693}{10.6 \times 60} \\ &= 0.00109 \text{ min}^{-1}\end{aligned}$$

$$\begin{aligned}\therefore t_{\max} &= \frac{2.303}{(0.01145 - 0.00109)} \log \left( \frac{0.01145}{0.00109} \right) \\ &= 227 \text{ min}\end{aligned}$$

**Problem 19.** An isotopic species of lithium hydride  $^6\text{Li}^2\text{H}$  is a potential nuclear fuel, on the basis of the reaction



Calculate the expected power production in MW, associated with  $1.00 \text{ g}$  of  $^6\text{Li}^2\text{H}$  per day (process is 100% efficient).

[ $^6_3\text{Li} = 6.01512 \text{ u}$ ,  $^2_1\text{H} = 2.01410 \text{ u}$ ,  $^4_2\text{He} = 4.00260 \text{ u}$ ],  $\text{u}$  is amu and  $1 \text{ u} = 931 \text{ MeV}$

**Plan** Energy =  $\Delta m \times c^2$ ,  $1 \text{ MW} = 10^6 \text{ W} = 10^6 \text{ J s}^{-1}$   
Thus, energy in MW can be calculated.

$$\begin{aligned}\text{Solution } \Delta m &= \text{mass decay} = m(^6_3\text{Li}) + m(^2_1\text{H}) - 2m(^4_2\text{He}) \\ &= (6.01512 + 2.01410) - 2 \times 4.0026 \\ &= 0.02402 \text{ u}\end{aligned}$$

thus, energy of one atomic event (one mass decay)

$$\begin{aligned}&= 0.0240 \times 931 \times 10^6 \text{ eV} \\ &= 0.0240 \times 931 \times 10^6 \times 1.6 \times 10^{-19} \text{ J} \\ &= 3.59 \times 10^{-12} \text{ J}\end{aligned}$$

energy per mol of  $\text{LiH} = 3.59 \times 10^{-12} \times 6.02 \times 10^{23}$

$$= 2.16 \times 10^{12} \text{ J mol}^{-1}$$

$$\text{energy per g of LiH} = \frac{2.16 \times 10^{12}}{8} \text{ J g}^{-1}$$

$$\text{energy per g of LiH per second} = \frac{2.16 \times 10^{12}}{8 \times 24 \times 3600} \text{ J g}^{-1} \text{ s}^{-1}$$

$$\begin{aligned}&= 3.125 \times 10^6 \text{ J s}^{-1} \text{ g}^{-1} \\ &= 3.125 \times 10^6 \text{ W g}^{-1} \quad (\text{Js}^{-1} = 1 \text{ W}) \\ &= 3.125 \text{ MW g}^{-1} \quad (1 \text{ MW} = 10^6 \text{ W})\end{aligned}$$

**Problem 20.** Tritium, or hydrogen-3, is formed in the upper atmosphere by cosmic rays, similar to the formation of C-14. Tritium has been used to determine the age of wines. A certain wine that has been aged in a bottle has a tritium content only 78% of that in a similar wine of the same mass that has just been bottled. How long has the aged wine been in the bottle?  $T_{50}$  of tritium is 12.2 years.

$$\text{Plan Use } \lambda = \frac{2.303}{t} \log \frac{N_0}{N} \text{ and } \lambda = \frac{0.693}{T_{50}}$$

Thus, time  $t$  can be calculated.

$$\begin{aligned}\text{Solution } \lambda &= \frac{2.303}{t} \log \frac{N_0}{N} \\ \frac{0.693}{T_{50}} &= \frac{2.303}{t} \log \frac{N_0}{N} \\ \frac{0.693}{12.2} &= \frac{2.303}{t} \log \frac{100}{78} \\ \therefore t &= 4.375 \text{ years}\end{aligned}$$

**Problem 21.** When a positron and an electron collide, they are annihilated and two gamma photons of equal energy are emitted. Calculate the wavelength corresponding to this gamma emission:

**Plan** Energy per photon =  $m_e c^2$

$$\therefore E = h\nu = \frac{hc}{\lambda}$$

Thus,  $\lambda$  can be calculated.

**Solution**  ${}_1e^0 + {}_{-1}e^0 \longrightarrow 2$  gamma photons of equal energy

The energy of the above process is

$$\begin{aligned} E &= 2 m_e c^2 \\ &= 2 (9.11 \times 10^{-31} \text{ kg}) (3 \times 10^8 \text{ m s}^{-1})^2 \\ &= 1.6398 \times 10^{-13} \text{ J} \end{aligned}$$

energy of one photon =  $8.199 \times 10^{-14} \text{ J}$

$$\text{taking } E = \frac{hc}{\lambda}$$

$$\begin{aligned} \lambda &= \frac{hc}{E} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{8.199 \times 10^{-14}} \text{ m} \\ &= 2.42 \times 10^{-12} \text{ m} = 2.42 \text{ pm} \end{aligned}$$

**Problem 22.** Natural nitrogen is 99.63%  ${}^{14}\text{N}$  with mass 14.00307 amu and 0.37%  ${}^{15}\text{N}$ , with mass number 15.00011 amu. Which isotope is more stable,  ${}^{14}\text{N}$  or  ${}^{15}\text{N}$ ?

**Plan** Binding energy per nucleon =  $\frac{\Delta m (\text{amu}) \times 931}{\text{number of nucleons}}$

Isotope with larger binding energy per nucleon is more stable.

**Solution** There are 7n, 7p and 7e<sup>-</sup> in  ${}^{14}\text{N}$

$$\begin{aligned} \text{mass of nucleons} &= 7 \times 1.00782505 + 7 \times 1.008664904 \\ &= 14.11543 \text{ amu} \end{aligned}$$

$$\begin{aligned} \text{mass defect} &= 14.11543 - 14.00307 \\ &= 0.11236 \text{ amu} \end{aligned}$$

$$\begin{aligned} \text{binding energy per nucleon} &= \frac{0.11236 \times 931}{14} \text{ MeV} \\ &= 7.472 \text{ MeV} \end{aligned}$$

There are 8n, 7p and 7e<sup>-</sup> in  ${}^{15}\text{N}$

$$\begin{aligned} \text{mass of nucleons} &= 8 \times 1.008664904 + 7 \times 1.00782505 \\ &= 15.12409 \text{ amu} \end{aligned}$$

$$\begin{aligned} \text{mass defect} &= 15.12409 - 15.00011 \\ &= 0.12398 \text{ amu} \end{aligned}$$

$$\begin{aligned} \text{binding energy per nucleon} &= \frac{0.12398 \times 931}{15} \text{ MeV} \\ &= 7.695 \text{ MeV} \end{aligned}$$

As binding energy per nucleon is larger for  ${}^{15}\text{N}$ , hence,  ${}^{15}\text{N}$  is more stable.

**Problem 23.** What is the change in mass (in grams) when 2 mol of hydrogen atoms combine to form 1 mol of hydrogen molecule?

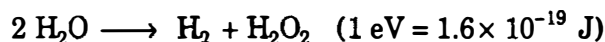


**Plan** The problem asks us to calculate the mass defect  $\Delta m$  when the energy change  $\Delta E$  is known. To do this, we have to rearrange the Einstein equation to solve for mass, remembering that  $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$ .

**Solution**  $\Delta E = \Delta mc^2$

$$\begin{aligned} \Delta m &= \frac{\Delta E}{c^2} = \frac{-436 \text{ kJ}}{(3 \times 10^8)^2 \text{ m}^2 \text{ s}^{-2}} \\ &= \frac{-436 \times 10^3 \text{ J}}{9 \times 10^{16} \text{ m}^2 \text{ s}^{-2}} \\ &= \frac{-436 \times 10^3 \text{ kg m}^2 \text{ s}^{-2}}{9 \times 10^{16} \text{ m}^2 \text{ s}^{-2}} \\ &= -4.84 \times 10^{-12} \text{ kg} \end{aligned}$$

**Problem 24.** Calculate the volume of  $\text{H}_2$  gas at STP which would be produced per minute from radiolysis of water in a 1000 kW reactor, assuming that 100 eV of energy produces 1 molecule of hydrogen



**Plan** Energy given in kW is to be converted into  $\text{J s}^{-1}$  and thus, volume of  $\text{H}_2$  gas produced in this reactor can be calculated.

**Solution** Given  $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$

$$\begin{aligned} \therefore 100 \text{ eV} &= 100 \times 1.6 \times 10^{-19} \text{ J} \\ &= 1.6 \times 10^{-17} \text{ J} \end{aligned}$$

$$\begin{aligned} \text{Also } 1000 \text{ kW} &= 1000 \times 1000 \text{ W} \\ &= 1000 \times 1000 \text{ J s}^{-1} \\ &= 10^6 \text{ J s}^{-1} \\ &= 10^6 \times 60 \text{ J in one minute} \end{aligned}$$

(as required)

$$1.6 \times 10^{-17} \text{ J produces} = 1 \text{ molecule of } \text{H}_2$$

$$\begin{aligned} \therefore 60 \times 10^6 \text{ J produces} &= \frac{60 \times 10^6}{1.6 \times 10^{-17}} \text{ molecules} \\ &= 37.5 \times 10^{23} \text{ molecules} \\ &= \frac{37.5 \times 10^{23}}{6.02 \times 10^{23}} \text{ mol } \text{H}_2 \\ &= 6.23 \text{ mol } \text{H}_2 \end{aligned}$$

$$1 \text{ mol at STP has volume} = 22.4 \text{ L}$$

$$\therefore 6.23 \text{ mol at STP has volume} = 139.55 \text{ L}$$

# Master Exercises

## Exercise 1 (Stage 1 : Learning)

### Analytical Questions

#### Theory of Radioactive Disintegration

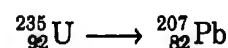
1. Half-life of  $^{221}\text{Fr}$  is 4.8 min. If 1 mg of the isotope is isolated, how much will remain after (a) 19.2 min (b) 48 min?
2. 0.1 mg of  $^{239}\text{Pu}$  emits  $1.4 \times 10^7$  particles per minute. What is its half-life?
3. A radioactive isotope has a half-life of 14.8 hr. How much time it will take for the activity to drop to (a) 10 per cent, (b) 5 per cent of its original value?
4. Radioactive equilibrium is established in a uranium mineral between radium and uranium atoms in the ratio 1 : 28. If half-life period of radium is 1620 years, calculate the disintegration constant of uranium.
5. 1 g of  $^{226}\text{Ra}$  emits  $11.6 \times 10^{17}$   $\alpha$ -particles in a year. If  $\lambda = 4.353 \times 10^{-4} \text{ year}^{-1}$ , calculate the value of Avogadro's number.
6. Calculate the mass of  $^{14}\text{C}$  ( $T_{50} = 5720$  years) atom which has radioactivity of 1 mCi.
7. The half-life of  $^{40}\text{K}$  is  $1.28 \times 10^9$  years. What mass of this nuclide has an activity of  $1.00 \mu\text{Ci}$ ?
8.  $^{210}_{84}\text{Po}$  decays with  $\alpha$ -particle to  $^{206}_{82}\text{Pb}$  with a half-life of 138.4 days. If 1.0 g of  $^{210}_{84}\text{Po}$  is placed in a sealed tube how much of helium will accumulate in 69.2 days? Express the answer in  $\text{cm}^3$  at STP.
9. 10 g atoms of an  $\alpha$ -active radioactive isotope are disintegrating in a sealed container. In one hour, the He gas collected at STP is  $11.2 \text{ cm}^3$ . Calculate half-life of radioactive isotope.
10. 0.1 g atom of radioactive isotope  $^A_Z\text{X}$  (half-life 5 days) is taken. How many number of atoms will decay during eleventh day.
11. A certain radioisotope  $^A_Z\text{X}$  ( $T_{50} = 10$  days) decays to give  $^A_{Z-2}\text{Y}$ . If one g atom of  $^A_Z\text{X}$  is kept in a sealed

vessel, how much He will accumulate in 20 days at STP?

12. The disintegration rate of a certain radioactive sample at any instant is 4750 dpm (disintegration per minute). Five minutes later, the rate becomes 2700 dpm. Calculate half-life of sample.
13. Chlorine-34 has a half-life of only 1.53 s. How long does it take for 99.99% of a  $^{34}\text{Cl}$  sample to decay?

#### Nuclear stability and Nuclear Reactions

14. Calculate the number of  $\alpha$  and  $\beta$ -particles in the change :



15. 1 g of  $^{198}_{79}\text{Au}$  ( $T_{50} = 65$  h.) decays by  $\beta$ -emission to produce stable Hg.  
(a) Write nuclear reaction for process.  
(b) How much Hg will be present after 260 h?
16.  $^{238}_{92}\text{U}$  is radioactive and it emits  $\alpha$  and  $\beta$ -particles to form  $^{206}_{82}\text{Pb}$ . Calculate the number of  $\alpha$  and  $\beta$ -particles emitted in this conversion. An ore of  $^{238}_{92}\text{U}$  is found to contain  $^{238}_{92}\text{U}$  and  $^{206}_{82}\text{Pb}$  in the weight ratio of 1 : 0.1. The half-life period of  $^{238}_{92}\text{U}$  is  $4.5 \times 10^9$  years. Calculate the age of the ore.
17. (a) The super heavy element  $^{287}\text{Uuq}$  was made by firing a beam of  $^{40}\text{Ca}$  ions at  $^{240}\text{Pu}$ . Three neutrons were ejected in the reaction. Write a balanced nuclear equation for the synthesis of  $^{287}\text{Uuq}$ .  
(b) Boron is an effective absorber of neutrons. When boron-10 adds a neutron, an  $\alpha$ -particle is emitted. Write an equation for this nuclear reaction.

#### Binding Energy

18. Calculate the mass defect and binding energy in  
(a)  $^{10}_5\text{B}$  (isotopic mass = 10.01019 amu) and  
(b)  $^7_3\text{Li}$  (isotopic mass = 7.01436 amu).

- The alpha-particles emitted by radium have energies of 4.795 MeV and 4.611 MeV. What is the wavelength of the gamma ray associated with the decay?
- What is the wavelength (in nm) of gamma-rays whose energy is 1.50 eV?
- Calculate the mass defect (in g/mol) and the binding energy (in MeV/nucleon) for the following nuclides. Which of the two is more stable?  
(a)  $^{50}\text{Cr}$  (atomic mass = 49.94605 amu)  
(b)  $^{64}\text{Zn}$  (atomic mass = 63.92915 amu)
- The atomic mass of  $^{16}\text{O}$  is  $15.995 m_u$  while the individual masses of proton and neutron are 1.0073 and  $1.0087 m_u$ . The mass of electron =  $0.000548 m_u$ . Calculate the binding energy of the oxygen nucleus in joules.
- The isotopic masses of  $^2_1\text{H}$  and  $^4_2\text{He}$  are 2.0141 and  $4.0026 m_u$  respectively and the velocity of light in vacuum is  $2.998 \times 10^8 \text{ ms}^{-1}$ . Calculate the quantity of energy (in J) liberated when two moles of  $^2_1\text{H}$  undergoes fusion to form one mole of  $^4_2\text{He}$ .
- The radioactive isotope  $^{60}_{27}\text{Co}$  which has now replaced radius in the treatment of cancer can be made by a  $(n, p)$  or  $(n, \gamma)$  reaction. For each reaction, indicate the appropriate target nucleus. If the half-life of  $^{60}_{27}\text{Co}$  is 7 yr, evaluate the decay constant in  $\text{s}^{-1}$ .
- A piece of wood from an archaeological source shows a  $^{14}\text{C}$  activity which is 60% of the activity found in fresh wood today. Calculate the age of the archaeological sample. ( $t_{1/2} = C = 5770 \text{ yr}$ )
- Calculate the mass of  $^{140}\text{La}$  in a sample whose activity is  $3.7 \times 10^{10} \text{ Bq}$  (1 becquerel,  $\text{Bq} = 1$  disintegration per second) given that its  $t_{1/2}$  is 40 hr.
- Calculate the binding energy per nucleon for  $^{12}\text{C}$ ,  $^{14}\text{N}$ ,  $^{16}\text{O}$ , and comment on their relative magnitudes. Masses of proton and neutron are 1.0078 and  $1.0087 m_u$  respectively. ( $1 m_u = 931 \text{ MeV}$ )

### Applications

- A sample of uranium ore was found to contain 0.28 g  $^{206}\text{Pb}$  and 1.67 g of  $^{238}\text{U}$ . Assuming that all Pb came from the decay of  $^{238}\text{U}$ , what is the age of the ore? (Given  $T_{50}$  of  $^{238}\text{U}$  is  $4.51 \times 10^9$  years).
- A sample of  $^{238}\text{U}$  (half-life =  $4.5 \times 10^9$  years) ore is found to contain 23.8 g of  $^{238}\text{U}$  and 20.6 g of  $^{206}\text{Pb}$ . Calculate the age of the ore.

### NCERT Problems

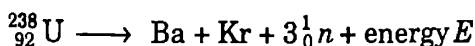
- What is meant by nuclear binding energy? Calculate the binding energy per nucleon of Li isotope, which has the isotopic mass of  $7.016 m_u$ . The individual masses of neutron and proton are  $1.008665 m_u$  and  $1.007277 m_u$ , respectively and the mass of electron =  $0.000548 m_u$ .

## Exercise 2

### (Stage 2 : High Skill Problem Solving)

#### Only One Option Correct

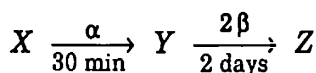
- In the chain reaction



neutrons and energy produced at  $n$ th step will be:

- $3n, nE$
- $3^n, nE$
- $3^n, 3^{n-1} E$
- $3^{n-1}, nE$

- A radioactive element decays by the sequence, and with half-lives, given below :



Which of the following statements about this system are correct ?

- After two hours, less than 10% of the initial X is left
- Maximum amount of Y present at any time before 30 min is less than 50% of the initial amount of X
- Atomic number of X and Z are same
- All of the above

- $^{27}_{13}\text{Al}$  is a stable isotope.  $^{29}_{13}\text{Al}$  is expected to disintegrate by  
(a)  $\alpha$ -emission (b)  $\beta$ -emission  
(c) positron emission (d) neutron emission
- The number of  $\alpha$  and  $\beta$  particles lost when  $^{238}_{92}\text{U}$  changes to  $^{206}_{82}\text{Pb}$  are  
(a)  $8\alpha, 6\beta$  (b)  $6\alpha, 8\beta$   
(c)  $6\alpha, 6\beta$  (d)  $8\alpha, 8\beta$
- Assuming that only particles emitted from atoms during natural radioactive decay are  $\alpha$  and  $\beta$ -particles, which of the following atoms could not possibly result from the natural decay of  $^{235}_{92}\text{U}$   
(a)  $^{231}_{89}\text{Ac}$  (b)  $^{227}_{89}\text{Ac}$   
(c)  $^{225}_{89}\text{Ac}$  (d)  $^{207}_{82}\text{Pb}$
- Of the following types of radiations, the only one to be deflected in a magnetic field is  
(a) X-ray (b)  $\gamma$ -ray  
(c)  $\beta$ -ray (d) neutrons

7. A process that produces a one-unit increase in atomic number is  
 (a) electron capture (b)  $\beta^-$ -emission  
 (c)  $\alpha$ -emission (d)  $\gamma$ -ray emission
8. Of the following nuclides, the one most likely to be radioactive is  
 (a)  $^{31}_{15}\text{P}$  (b)  $^{66}_{30}\text{Zn}$   
 (c)  $^{14}_7\text{N}$  (d)  $^{14}_6\text{C}$
9. One of the following elements has eight naturally occurring stable isotopes  
 (a) Ra (b) Au  
 (c) Cd (d) Br
10. Of the following nuclides, the one most likely to decay by positron ( $\beta^+$ ) emission is  
 (a)  $^{59}\text{Cu}$  (b)  $^{63}\text{Cu}$   
 (c)  $^{67}\text{Cu}$  (d)  $^{68}\text{Cu}$
11. Among the following nuclides, the highest binding energy per nucleon is found for  
 (a)  $^3_1\text{H}$  (b)  $^{16}_8\text{O}$   
 (c)  $^{56}_{26}\text{Fe}$  (d)  $^{235}_{92}\text{U}$
12. The most radioactive of the isotopes of an element is the one with the largest value of its  
 (a) half-life (b) neutron number  
 (c) atomic number (d) decay constant
13. The radiation that produces the greatest number of ions as it passes through matter is  
 (a)  $\alpha$  (b)  $\gamma$   
 (c)  $\beta^-$  (d)  $\beta^+$
14. The type of radiation that has the greatest penetrating power through matter is  
 (a)  $\alpha$  (b)  $\gamma$   
 (c)  $\beta^-$  (d) visible light
15. In uranium mineral, the atomic ratio  $N_{\text{U-238}} / N_{\text{Pb-206}}$  is nearly equal to one. The age (in years) of the mineral is nearly (half-life period of U-238 is  $4.5 \times 10^9$  years)  
 (a)  $3.0 \times 10^8$  (b)  $4.5 \times 10^9$   
 (c)  $3.0 \times 10^9$  (d)  $4.5 \times 10^8$
16. For an  $\alpha$ -emitting isotope, the value of disintegration constant is  $0.49 \times 10^{-10}$  per year. The amount of the isotope of a given sample will reduce to half its value after a period (in years) of nearly  
 (a)  $0.45 \times 10^{10}$  (b)  $0.9 \times 10^{10}$   
 (c)  $1.41 \times 10^{10}$  (d)  $2.82 \times 10^{10}$
17. In nuclear reaction



the mass loss is nearly 0.02 amu. Hence, the energy released (in units of million kcal/mol) in the process is approximately

- (a) 430 (b) 220  
 (c) 120 (d) 50

18. Consider the following nuclear reactions

1.  $^{14}_7\text{N} + ^4_2\text{He} \longrightarrow ^{17}_8\text{O} + ^1_1\text{H}$
2.  $^9_4\text{Be} + ^1_1\text{H} \longrightarrow ^6_3\text{Li} + ^4_2\text{He}$
3.  $^{24}_{12}\text{Mg} + ^4_2\text{He} \longrightarrow ^{27}_{14}\text{Si} + ^1_0\text{n}$
4.  $^{10}_5\text{B} + ^4_2\text{He} \longrightarrow ^{13}_7\text{N} + ^1_0\text{n}$

Examples of induced radioactivity would include reactions:

- (a) 3 and 4 (b) 1 and 2  
 (c) 1, 3 and 4 (d) 1, 2, 3 and 4

19. Match list I with list II and select the correct answer, using the codes given :

| List I              | List II                                              |
|---------------------|------------------------------------------------------|
| A. $^{32}\text{P}$  | 1. Location of tumour in brain                       |
| B. $^{24}\text{Na}$ | 2. Location of blood clots and circulatory disorders |
| C. $^{60}\text{Co}$ | 3. Radio-therapy                                     |
| D. $^{131}\text{I}$ | 4. Agriculture research                              |

#### Codes

- |     |   |   |   |   |
|-----|---|---|---|---|
|     | A | B | C | D |
| (a) | 4 | 1 | 2 | 3 |
| (b) | 4 | 3 | 2 | 1 |
| (c) | 4 | 2 | 3 | 1 |
| (d) | 3 | 1 | 2 | 4 |

20. Aluminium-25 decays by emitting a positron. The species immediately produced has  
 (a)  $12p, 13n, 13e^-$  (b)  $13p, 12n, 13e^-$   
 (c)  $12p, 13n, 12e^-$  (d)  $14p, 11n, 14e^-$
21. The half-life of  $^{99}\text{Tc}$  is 6.0 h. Hence, average life is  
 (a) 4.17 h (b) 3.0 h  
 (c) 8.66 h (d) 8.00 h
22. Tritium,  $^3_1\text{H}$  has a half-life of 12.26 years. A 5.00 mL sample of tritiated water has an activity of  $2.40 \times 10^9$  cpm. How many years will it take for the activity to fall to  $3.00 \times 10^8$  cpm?  
 (a) 6.13 (b) 12.26  
 (c) 24.52 (d) 36.78
23. In a series of three steps in radioactive disintegration sequence starting with  $^{228}_{88}\text{Ra}$ , the particles emitted are, successively,  $\beta^-$ ,  $\beta^-$  and  $\alpha$ -particles. The resulting product is an isotope of  
 (a)  $^{92}\text{U}$  (b)  $^{90}\text{Th}$   
 (c)  $^{88}\text{Ra}$  (d)  $^{86}\text{Rn}$
24. 1 g of  $^{200}_{79}\text{Au}$  ( $T_{50} = 13$  days) emits a  $\beta$ -particle forming a stable Hg atom. Hg formed at the end of 52 days  
 (a) 0.0625 g (b) 0.9375 g  
 (c) 0.7500 g (d) 0.2500 g

25. At radioactive equilibrium, the ratio between the atoms of two radioactive elements  $A$  and  $B$  was found to be  $3.1 \times 10^9 : 1$  respectively. If  $T_{50}$  of the element  $A$  is  $2 \times 10^{10}$  yrs, then  $T_{50}$  of the element  $B$  is  
 (a)  $6.2 \times 10^9$  yr (b) 6.45 yr  
 (c)  $2 \times 10^{10}$  yr (d)  $3.1 \times 10^9$  yr
26. Weight of  $^{14}\text{C}$  to have radioactivity 1 curie [ $\lambda$  (disintegration constant) =  $4.4 \times 10^{-12} \text{ s}^{-1}$ ] is  
 (a)  $2 \times 10^{-4}$  kg (b)  $0.9 \times 10^{-4}$  kg  
 (c)  $1.7 \times 10^{-4}$  kg (d)  $3.7 \times 10^{-10}$  kg
27. If half-life period is 100 yr, average life is nearly  
 (a) 100 yr (b) 70 yr  
 (c) 144 yr (d) 90 yr
28. There are  $0.618 \mu\text{g}$  of  $^{206}\text{Pb}$  and  $0.238 \mu\text{g}$  of  $^{238}\text{U}$  in a rock. If  $T_{50}$  of  $^{238}\text{U}$  is  $1.5 \times 10^9$  yr, age of the rock is  
 (a)  $1.5 \times 10^9$  yr (b)  $3.0 \times 10^9$  yr  
 (c)  $4.5 \times 10^9$  yr (d)  $0.75 \times 10^9$  yr
29.  $A \xrightarrow[T_A]{k_A}$  product,  $B \xrightarrow[T_B]{k_B}$  product  
 $A$  and  $B$  are two radioactive elements with half-life periods  $T_A$  and  $T_B$  (in years) and  $k_A(\text{yr}^{-1})$  and  $k_B(\text{atom}^{-1} \text{ year}^{-1})$ . If half-life periods are equal, disintegration rate at the start of disintegration would be  
 (a)  $k_A T_A$  (b) 0.693  
 (c) both (a) and (b) (d) None of these
30. Which of the following nuclear reactions is an example of nuclear fusion?  
 (a)  $^{12}_6\text{C} + ^1_1\text{H} \longrightarrow ^{13}_7\text{N} + \gamma$   
 (b)  $^{14}_7\text{N} + ^1_0\text{n} \longrightarrow ^{12}_6\text{C} + ^1_1\text{H}$   
 (c)  $^2_1\text{H} + ^3_1\text{H} \longrightarrow ^4_2\text{He} + ^1_0\text{n}$   
 (d)  $^{235}_{92}\text{U} + ^1_0\text{n} \longrightarrow ^{142}_{56}\text{Ba} + ^{91}_{36}\text{Kr} + 3^1_0\text{n}$
31. Match list I with list II and select the correct answer:
- | List I<br>(Isotope)       | List II<br>(Characteristic)    |
|---------------------------|--------------------------------|
| A. $^{40}_{20}\text{Ca}$  | 1. unstable, $\alpha$ -emitter |
| B. $^{133}_{53}\text{I}$  | 2. unstable, $\beta$ -emitter  |
| C. $^{121}_{53}\text{I}$  | 3. unstable, positron emitter  |
| D. $^{232}_{90}\text{Th}$ | 4. stable                      |
- (a) A B C D  
 (b) 1 2 3 4  
 (c) 4 3 2 1  
 (d) 4 2 3 1
32. In the esterification of an organic acid  $R\text{---COOH}$  by alcohol  $R'\text{OH}$ , O of acid is isotopic.  

$$R\text{---}\overset{\text{O}}{\parallel}\text{C}\text{---}^{18}\text{OH} + R'\text{---O---H} \longrightarrow R\text{---}\overset{\text{O}}{\parallel}\text{C}\text{---OR}' + \text{H}_2\text{O}$$
  
 Which of the following statement is correct?  
 (a)  $^{18}\text{O}$  is in ester  
 (b)  $^{18}\text{O}$  is in water  
 (c)  $^{18}\text{O}$  is in both  
 (d)  $^{18}\text{O}$  is in none
33. Thiosulphate ion,  $\text{S}_2\text{O}_3^{2-}$  on acidification changes to  $\text{SO}_2$  along with precipitation of sulphur  

$$^{35}\text{S}^{32}\text{SO}_3^{2-} + 2\text{H}^+ \longrightarrow \text{H}_2\text{O} + \text{SO}_2 + \text{S}$$
  
 Which is correct statement?  
 (a)  $^{35}\text{S}$  is in sulphur (b)  $^{35}\text{S}$  is in  $\text{SO}_2$   
 (c)  $^{35}\text{S}$  is in both (d)  $^{35}\text{S}$  is in none
34. Water used as moderator in nuclear reactor is called  
 (a) heavy water (b) hard water  
 (c) nuclear water (d) critical water
35.  $^{14}_7\text{N} + ^1_0\text{n} \longrightarrow ^{14}_6\text{C} + ^1_1\text{H}$  is written as  
 (a)  $^{14}_7\text{N} (n, e) ^1_1\text{H}$  (b)  $^{14}_7\text{N} (p, n) ^{14}_6\text{C}$   
 (c)  $^{14}_7\text{N} (n, p) ^{14}_6\text{C}$  (d)  $^{14}_6\text{C} (p, n) ^{14}_7\text{N}$
36.  $^{238}_{92}\text{U}$  (III B) emits two  $\alpha$ -particles; new element will be placed in  
 (a) VII B (b) VII A  
 (c) II A (d) II B
37. After the emission of a  $\beta$ -particle followed by  $\alpha$ -particle from  $^{214}_{83}\text{Bi}$ , the number of neutrons in the atom is  
 (a) 130 (b) 129  
 (c) 128 (d) 127
38. Which of the following are fissile isotopes?  
 I.  $^{238}_{92}\text{U}$  II.  $^{233}_{92}\text{U}$   
 III.  $^{239}_{94}\text{Pu}$  IV.  $^{232}_{90}\text{U}$   
 Select the correct answer from the following  
 (a) I and II (b) II and III  
 (c) I and IV (d) All of these
39.  $^{23}\text{Na}$  is the more stable isotope of Na.  $^{24}_{11}\text{Na}$  can undergo radioactive decay by  
 (a)  $\beta^-$ -emission  
 (b)  $\alpha$ -emission  
 (c)  $\beta^+$ -emission  
 (d) K-electron capture
40. The missing fission product in the reaction  

$$^{235}_{92}\text{U} + ^1_0\text{n} \longrightarrow ^{146}_{57}\text{La} + \dots + 3^1_0\text{n}$$
 is  
 (a)  $^{86}_{35}\text{Br}$  (b)  $^{87}_{35}\text{Br}$   
 (c)  $^{89}_{35}\text{Br}$  (d)  $^{89}_{32}\text{Ge}$

41. Which is the correct combination?

| Change in     |               |             |                |  |
|---------------|---------------|-------------|----------------|--|
| Emission      | Atomic number | Mass number | Neutron number |  |
| (a) $\alpha$  | -2            | -2          | -2             |  |
| (b) $\beta^-$ | +1            | 0           | -1             |  |
| (c) $\gamma$  | 0             | 0           | -1             |  |
| (d) $\beta^+$ | -1            | 0           | 0              |  |

42. Match the radioisotopes with their applications from the alternates given.

| Radioisotopes     | Applications             |
|-------------------|--------------------------|
| I. Cobalt-60      | 1. Leukemia therapy      |
| II. Potassium-40  | 2. Thyroid therapy       |
| III. Iodine-123   | 3. Geological dating     |
| IV. Phosphorus-32 | 4. Cancer therapy        |
| V. Carbon-14      | 5. Archaeological dating |

|     | I | II | III | IV | V |
|-----|---|----|-----|----|---|
| (a) | 1 | 2  | 3   | 4  | 5 |
| (b) | 5 | 4  | 3   | 2  | 1 |
| (c) | 4 | 3  | 2   | 1  | 5 |
| (d) | 4 | 3  | 2   | 5  | 1 |

43. Constituents of wine are carbon, hydrogen and oxygen. Half-lives of  $^{13}\text{C}$ ,  $^{15}\text{O}$  and  $^3\text{H}$  are respectively 5730 years, 124 s and 12.5 years. A bottle of wine was sealed about 6 years ago. To confirm its age, which of the isotopes would you choose to determine its age?

- (a)  $^{13}_6\text{C}$  (b)  $^{15}_8\text{O}$   
(c)  $^3_1\text{H}$  (d) Any of these

44. 'Fat man' relates to

- (a) Pu bomb  
(b) U bomb  
(c) Th bomb  
(d) literary word from a book

45. 'Little boy' relates to

- (a) Pu bomb (b) U bomb  
(c) H bomb (d) He bomb

46. Thorium is found in

- (a) pitchblende (b) uranite  
(c) monazite (d) malachite green

47. Consider following statements

- I. 'Carbon-dating' is based on the measurement of activity of  $^{14}\text{C}$   
II.  $^{40}\text{K}$  is used to determine age of the objects upto 1 million years old  
III. The uranium-lead method is based on the natural uranium-238 decay series which ends up with the production of stable lead-206.

Select correct statements.

- (a) I, II (b) II, III  
(c) I, III (d) I, II, III

48. Beta-emission takes place

- (a) from the elements above the band of stability  
(b) when neutron is converted to proton  
(c) with shifting of the new element one group towards right  
(d) following all the facts given above

49. Mass defect of 1 g gives energy equal to

- (a)  $9 \times 10^{13} \text{ J}$   
(b)  $5.625 \times 10^{32} \text{ eV}$   
(c) both (a) and (b)  
(d) None of the above

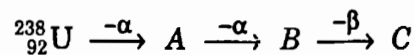
50. Select correct alternate.

- (a)  $^1_1\text{p} \longrightarrow ^1_0\text{n}$  is positron emission  
(b)  $^1_1\text{p} \longrightarrow ^1_0\text{n}$  is K-electron capture  
(c) both (a) and (b)  
(d) None of the above

## One or More Than One Options Correct

- Carbon-14 dating method is based on the fact that
  - carbon-14 fraction is same in all objects
  - carbon-14 is highly insoluble
  - ratio of carbon-14 and carbon-12 remains constant during disintegration
  - carbon-14 is highly soluble
- Select correct statement(s).
  - $^{131}\text{I}$  is used for the treatment of thyroid cancer
  - $^{59}\text{Co}$  cannot be used for treatment of cancer
  - $^{33}\text{P}$  is used for treatment of leukemia
  - excessive use of radioactive elements causes cancer
- Radioactive disintegration rate is affected by
  - temperature
  - pressure
  - electric field
  - None of these

4.  $^{238}_{92}\text{U}$  (III B) undergoes follows emissions



Which is/are correct statements?

- A will be of IB group
  - A will be of IIIB group
  - B will be of IIA (alkaline earth metal) group
  - C will be of IIIA (boron family) group
- Beta-emission takes place
    - from the elements above the band of stability
    - when neutron is converted to proton
    - such that new element remains in the same group
    - such that atomic number of the element formed increases by one unit
  - Mass defect of 1 g gives energy equal to
    - $9 \times 10^{13} \text{ J}$
    - $5.625 \times 10^{32} \text{ eV}$
    - $2.15 \times 10^{10} \text{ kcal}$
    - $9 \times 10^6 \text{ ergs}$

- Target nucleus  $A$  is converted to product nucleus  $B$  by  $(p, n)$  as:  $A(p, n)B$   
In this case  
(a)  $A$  and  $B$  are isotopes  
(b)  $A$  and  $B$  are isobars  
(c)  $A$  and  $B$  are isotones  
(d)  $B$  has higher atomic number than that of  $A$
- In a nuclear reactor, oxides of which of the following metals are used as fuel material?  
(a) Uranium (b) Thorium  
(c) Actinium (d) Plutonium
- Two radioactive substances  $X$  and  $Y$  have disintegration constant in the ratio  $2:1$ . If half-life of  $Y$  is 4 days then after 12 days starting with equal mole fraction of each in mixture of  $X$  and  $Y$   
(a) mole fraction of  $X$  and  $Y$  remains unchanged  
(b) mole fraction of  $X$  is larger than that of  $Y$   
(c) mole fraction of  $X$  is smaller than that of  $Y$   
(d) half-life of  $X$  is smaller than that of  $Y$
- Select correct statement(s).  
(a) Neutron-proton ratio after a nuclide,  $^{238}_{92}\text{U}$  loses an  $\alpha$ -particle is 1.6  
(b)  $^{27}_{13}\text{Al}$  can be converted to  $^{30}_{15}\text{P}$  by  $(\alpha, n)$  reaction  
(c) Nuclear fusion reactions are known as thermonuclear reactions  
(d) Larger the value of disintegration constant, greater the stability of radioactive element
- What mass of  $^{14}\text{C}$  with  $T_{50} = 5730$  years has activity equal to one curie?
- What is the wavelength (in nm) of gamma-rays whose energy is 1.50 eV?
- A positron has the same mass as an electron ( $9.109 \times 10^{-31}$  kg) but an opposite charge. When the two particles encounter each other, annihilation occurs and only gamma-rays are produced. How much energy (in  $\text{kJ mol}^{-1}$ ) is produced?
- Radiolysis of water yields hydrogen according to the reaction:  
$$2\text{H}_2\text{O} \longrightarrow \text{H}_2 + \text{H}_2\text{O}_2$$
  
Calculate the volume of hydrogen produced per hour in a 200 kW reactor. The yield of hydrogen is 1.7 molecules per 100 eV of energy absorbed.
- The nuclide  $^{50}_{21}\text{Sc}$ , mass 49.9516 amu, is neutron rich. It decays to form  $^{50}_{22}\text{Ti}$ , mass 49.94479 amu. If the emitted  $\beta^-$  particle has a kinetic energy of 0.80 MeV, what is the kinetic energy of the neutrino emitted simultaneously?
- How much of heat would be developed per hour from 1 Ci  $^{14}\text{C}$  source if all the energy of the  $\beta^-$  decay were imprisoned?
- In a thorium mineral the ratio by weight of  $^{208}\text{Pb}$  :  $^{232}\text{Th}$  is 0.2. The decay constant of  $^{232}\text{Th}$  is  $4.98 \times 10^{-11} \text{ year}^{-1}$ . Calculate the age of mineral.
- The activity of hair of an Egyptian mummy is 10  $\text{dismin}^{-1} \text{ g}^{-1}$  of  $^{14}\text{C}$ . What is the age of the mummy?  $T_{50}$  of  $^{14}\text{C}$  is 5730 years and disintegration rate of fresh sample of  $^{14}\text{C}$  is  $15 \text{ dismin}^{-1} \text{ g}^{-1}$ .
- 1 g of  $^{14}\text{C}$  from an archaeological sample gives 9.4  $\text{counts min}^{-1}$ . 1 g of  $^{14}\text{C}$  from a recently cut tree gives 15.3  $\text{counts min}^{-1}$  under the same conditions. How old is the archaeological sample? ( $T_{50}$  of  $^{14}\text{C}$  is 5730 years).
- Potassium-40 decays with a half-life of  $1.3 \times 10^9$  yr. What is the age of lunar rock sample that contains these isotopes in the ratio 34.1 atoms  $^{40}\text{K}$  : 65.9 atoms  $^{40}\text{Ar}$ ? Assume that no argon was originally in the sample and that none has been lost by weathering.
- $^{238}_{92}\text{U}$  by successive radioactive decays changes to  $^{206}_{82}\text{Pb}$ . A sample of uranium ore was analysed and found to contain 1.0 g  $^{238}\text{U}$  and 0.1 g  $^{206}\text{Pb}$ . Assuming that  $^{206}\text{Pb}$  has accumulated due to decay of  $^{238}\text{U}$ , find out the age of the ore.  $T_{50}$  of  $^{238}\text{U}$  is  $4.5 \times 10^9$  years.
- As a result of being exposed to the radiation released during the Japan nuclear accident in very recent Sunami, the dose of iodine-131 in a person's body is 7.4 mCi (1 mCi =  $1 \times 10^{-3}$  Ci). Calculate the number of atoms of iodine-131 ( $T_{50} = 8.1$  days).

## Brain Twisters

- An atomic battery operated with watch uses  $\beta$ -particles from  $^{147}_{61}\text{Pm}$  ( $T_{50} = 2.62$  yr) as the energy source. How long would it take for the rate of  $\beta$ -emission in the battery to be reduced to 5% of its original values?
- If 1 g of  $^{226}\text{Ra}$  emits  $11.6 \times 10^{17}$   $\alpha$ -particles in a year. If  $\lambda = 4.353 \times 10^{-4} \text{ yr}^{-1}$ , calculate value of Avogadro's number.
- One of the hazards of nuclear explosion is the generation of  $^{90}\text{Sr}$  and its subsequent incorporation in bones. This nuclide has a half-life of 28.1 years. Suppose one microgram ( $10^{-6}$  g) was absorbed by a new-born child, how much  $^{90}\text{Sr}$  will remain in his bones after 20 years?
- The activity of 30  $\mu\text{g}$  of  $^{247}\text{Cm}$  is 2.8 nCi ( $10^{-9}$  curie). Calculate the disintegration rate constant and the half-life of  $^{247}\text{Cm}$ .
- Upon irradiating californium with neutrons, a scientist discovered a new nuclide having mass number of 250 and a half-life of 0.50 h. Three hours after the irradiation, the observed radioactivity due to nuclide was 10 dis/min. How many atoms of the nuclide were prepared initially?



## Passage Comprehension Questions

### Passage 1

Back in 1953 the U.S. Army started an experimental programme of food irradiation so that deployed troops could have fresh food without refrigeration. The procedure is a simple one. Food is exposed to high levels of radiation to kill insects and harmful bacteria. It is then packaged in airtight containers, in which it can be stored for months without deterioration. The radiation sources for most food preservation are cobalt-60 and cesium-137, both of which are  $\gamma$ -emitters, although X-rays and electron beams can also be used to irradiate food.

Read the above passage and answer the following questions.

- The benefits of food irradiations are
  - it reduces energy demand by eliminating the need for refrigerations
  - it prolongs shelf life of various foods
  - both (a) and (b) are correct
  - None of the above is correct
- There have been certain objections against food preservation by irradiations. These are:
  - irradiated food may itself become radioactive
  - irradiation can destroy the nutrients such as vitamins and amino acids
  - ionising radiation produces reactive species such as the hydroxyl radical which then react with organic molecules to produce potentially harmful substances.
  - irradiated food may be much costlier
- Select correct statement(s).
  - A **rad** is a measure of the amount of high energy radiation absorbed by matter
  - 1 **rad** of  $\alpha$ -rays has the same effect on tissue as 1 **rad** of  $\gamma$ -rays
  - Iodine-131 can be used for scanning the thyroid for disorders
  - Strontium-90 is useful isotope for food radiation

### Passage 2

In a series of extraordinary events, a natural nuclear fission reactor operated at the time when the first life forms appeared on Earth. As is often the case in scientific endeavors, humans are not necessarily the innovators but merely the imitators of nature.

Read the above passage and answer the following questions.

- Nuclear-fission reaction is
  - chain reaction
  - induced by neutrons
  - related to Pu-bomb
  - related to U-bomb

- Select correct statements.

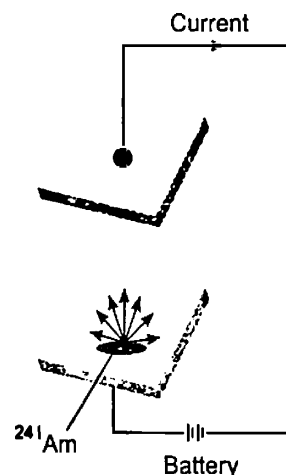
- Sr-90 and Cs-137 are the other by-products of nuclear fission released through bomb testing
- Sr-90 and Cs-137 can produce cancer of the bone
- Sr-90 like Ca is incorporated into bone and thus produces bone-cancer
- Cs-137 through radioactive, is rapidly eliminated from the tissue being quite soluble like K

### Passage 3

Read the following passage and answer the questions at the end.

A person received an anonymous gift of a decorative cube which he placed on his desk. A few months later he became ill and died shortly afterward. After investigation, the cause of his death was linked to the box. The box was air-tight and had no toxic chemicals on it. What might have killed the man?

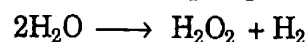
- $\alpha$ -rays emitting material
  - $\beta$ -rays emitting material
  - $\gamma$ -rays emitting material
  - KCN
- Am-241 is used in smoke detectors because it has a long half-life (458 y). Given the schematic diagram of a smoke detector below, explain how it works?



- it emits  $\alpha$ -particles which are energetic enough to ionise air molecules
- it emits  $\beta$ -particles which can complete the circuit
- it emits  $\gamma$ -particles which have high penetration
- it emits  $\alpha$ - and  $\beta$ -particles

### Passage 4

Radiolysis of water yields  $H_2$  as given below



In the analysis it is found that 1.7 molecules of  $H_2$  are yielded per 100 eV of energy absorbed. A nuclear power reactor of 200 kW capacity has been installed based on this reaction.

Read the above passage and answer the following questions.

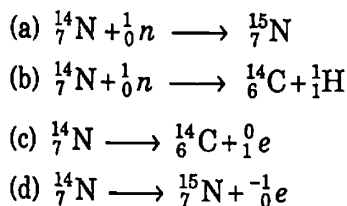
- Above reaction is an example of
  - disproportionation
  - redox
  - decomposition
  - displacement
- What mass of heavy water is required to yield 448 kL of heavy hydrogen at STP?
  - 996 kg
  - 448 kg
  - 800 kg
  - 720 kg
- Volume of  $H_2$  produced per minute in the above reactor is
  - 140 L
  - 70 L
  - 35 L
  - 28 L

### Passage 5

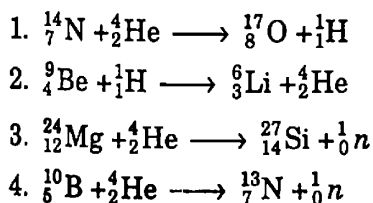
To detect bombs that may be smuggled into airplanes, the Federal Aviation Administration (FAA) will soon require all major airports in the United States to install thermal neutron analysers. The thermal neutron analyser will bombard baggage with low-energy neutrons, converting some of the nitrogen-14 nuclei to nitrogen-15, with simultaneous emission of  $\gamma$ -rays. Because nitrogen content is usually high in explosives, detection of a high dosage of  $\gamma$ -rays will suggest that a bomb may be present.

Read the above passage and answer the following questions.

- Nuclear process involves reaction



- Consider the following nuclear reactions



Examples of induced radioactivity would include reactions

- 3 and 4
- 1 and 2
- 1, 3 and 4
- 1, 2, 3 and 4

- The sensitivity of the neutral activation analysis depends on the

- neutron flux available for irradiation
- availability of nucleus to absorb a neutron
- energy of decay process
- All of the above are correct

- Select correct statement(s).

- Photon or particle is ionised and collected by the positive electrode in a Geiger counter
- A scintillation counter contains a phosphor, a substance that emits a flash of light when struck by a photon or particle
- Both of the above
- None of the above

### Passage 6

One of the products of radiation fall out from atmospheric bomb testing or nuclear accidents as at Chernobyl is iodine-131. People living in a region where iodine-131 was known to have been deposited were encouraged to use table salt enriched with non-radioactive isotope of iodine.

Read the above short write-up and answer the following questions.

- Non-radioactive isotope prescribed in the table-salt is

- I-130
- I-127
- I-132
- I-129

- The rate of iodine uptake by the thyroid is

- dependent upon the iodine concentration
- dependent upon pressure of iodine
- follows second-order kinetics
- independent of iodine concentration

- By use of non-radioactive iodine isotope in common salt

- rate of iodine-131 uptake is sharply reduced compared to uptake of iodine-127
- a new non-radioactive isotope is formed
- taste of table salt becomes better
- iodine-131 being water soluble is eliminated from tissue

### Passage 7

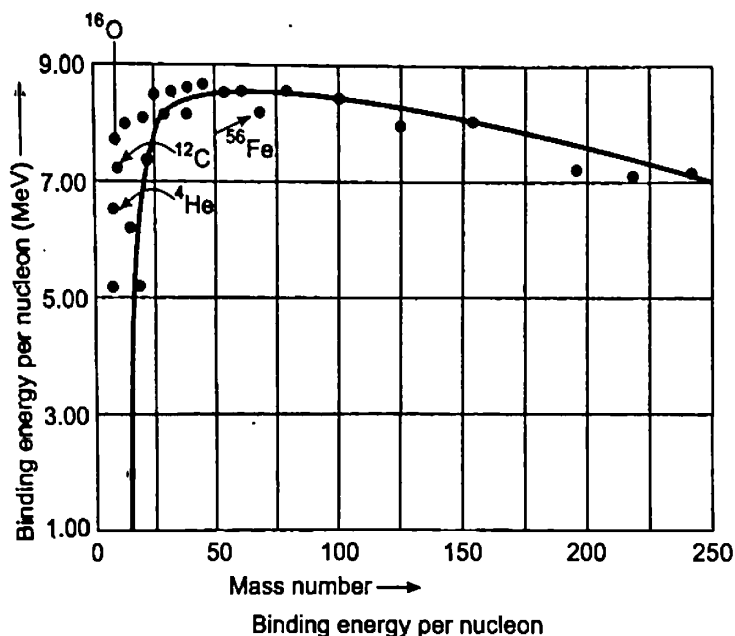
Read the following figure in paragraph and answer the questions at the end of it.

A number of basic questions have probably occurred to you as we have been describing nuclear decay processes.

Why do some radioactive nuclei decay by  $\alpha$ -emission and some by  $\beta^-$ -emission?

Why do the lighter elements have so few naturally occurring radioactive nuclides, whereas those of the heavier elements all seem to be radioactive?

Experimentally, it is found that nuclei with certain number of protons or neutrons appear to be very stable. These numbers called **magic numbers** and associated with specially stable nuclei, were later explained by the **shell model**.



- Which have comparatively higher energy?
  - Even number of protons and even number of neutrons
  - Even number of protons but odd number of neutrons
  - Even number of neutrons but odd number of protons
  - Odd number of protons as well as odd number of neutrons
- Magic number for protons are
  - 2, 8, 20, 28, 50, 126
  - 2, 8, 20, 28, 50, 82, 114
  - 2, 8, 20, 50, 82, 126
  - 1, 3, 5, 7, 9, 11
- Magic number for neutrons are
  - 1, 3, 9, 11, 13
  - 11, 19, 37, 55, 87
  - 2, 8, 20, 28, 50, 82, 126
  - 2, 8, 18, 36, 54, 86

### Passage 8

#### Don't Press the Panic Button.

Despite the crisis in Japan's Plants, India must not take nuclear power off the table.

Answer the following questions

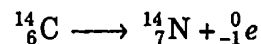
- In view of recent nuclear blasts due to Sunami in Japan countries are
  - going to stop nuclear-energy plan
  - devising methods to avoid this type of disaster
  - stressing thermal energy plan
  - stressing hydro-electric power
- Nuclear plan can't be taken off the table because of
  - unusual toxicity of the radioactive substance
  - technology outweighs such risks
  - nuclear power remains the only economically viable renewable source of energy
  - alternates (b) and (c)

### Assertion & Reason

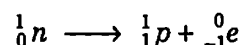
Codes :

- Both **A** and **R** are true and **R** is the correct explanation of **A**.
- Both **A** and **R** are true but **R** is not the correct explanation of **A**.
- A** is true but **R** is false.
- A** is false but **R** is true.

- Assertion (A)** : When there is emission of  $\beta$ -particle atomic number increases by one unit.



**Reason (R)** : Neutron is converted to proton



- Assertion (A)** : When there is an emission of  $\alpha$ -particle, new element is displaced two groups of the parent element.

**Reason (R)** : Atomic mass decreases by 2 units due to  $\alpha$ -particle emission.

- Assertion (A)** : Half-life period of the radioactive disintegration is independent of concentration.

**Reason (R)** : 75% disintegration takes place in a time twice the 50% disintegration.

- Assertion (A)** :  $\gamma$ -rays produce a greater health hazard to those who work with radioactive element.

**Reason (R)** :  $\gamma$ -rays are extremely penetrating high energy electromagnetic radiations.

- Assertion (A)** : Element formed by the successive emission of  $1\alpha$ -particle and  $2\beta$ -particles is placed in the same group as the parent element.

**Reason (R)** :  $\alpha$ -particle is  ${}^4_2\text{He}^{2+}$  while  $\beta$ -particle is  ${}^0_{-1}e$ .

- Assertion (A)** : Nuclear-fission is a chain reaction.

**Reason (R)** : Extra electrons formed in the intermediate steps further attack the nuclei.

### True & False

- A radioactive change is always irreversible and independent of temperature and pressure.
- Thorium (90) formed from emission of  $\alpha$ -particle from uranium (92, group IIIB) has been placed in group IIIB.
- Increase in atomic number by one unit due to emission of  $\beta$ -particle is as a result of conversion of neutron into proton.
- Successive emission of  $1\alpha$  and  $2\beta$ -particles results in the formation of isotopes.
- $\gamma$ -rays are not affected in magnetic or electric field.
- $\gamma$ -rays have least penetrating power.

- Nuclear-fusion chain initiation is endothermic and further reaction is also endothermic.
- D<sub>2</sub>O or graphite is a moderator in nuclear reactor.
- Elements with atomic number greater than 92 are called actinides.
- IUPAC representation of atomic number 108 is Uno.
- Ds is the latest IUPAC approved name of the element of atomic number 110.
- The more positive the packing fraction of an element, the more stable should be nucleus.
- Energy equivalent of 1 amu is 931 MeV.
- Age of earth is determined by Geological dating.
- MRI uses radio-waves.
- Iodine-131 is used in imaging the brain.
- $^{23}_{11}\text{Na}$  changes to  $^{24}_{12}\text{Mg}$  by bombardment of  $^1_0n$  and successive emission of  $\beta$ -particle.
- 'Fat man' relates to literary word from a book.
- $^{40}\text{K}$  is used to determine age of objects upto 1 million years old.
- 'Little boy' relates to U-bomb.

### Fill in the Blanks

- SI unit of radioactivity is ..... which is equal to ..... dps.
- Disintegration of  $3.7 \times 10^{10}$  atoms per second ( $3.7 \times 10^{10}$  dps) is called .....
- Successive emission of 1  $\alpha$ - and 2  $\beta$ -particles results in the formation of .....
- There is an increase in the atomic number by 1 unit due to .....
- $^{234}_{90}\text{Th}$  changes to  $^{206}_{82}\text{Pb}$  by emission of .....  $\alpha$ -particles and .....  $\beta$ -particles.
- Series                      Starts with                      Ends with  
(a)  $4n$                       ...                      ...  
(b)  $4n + 1$                       ...                      ...  
(c)  $4n + 2$                       ...                      ...  
(d)  $4n + 3$                       ...                      ...
- Radioactive disintegration follows ..... order kinetic.
- Radioactive change is ..... and independent of ..... and .....
- $k^{-1}$  ( $k$  is radioactive disintegration constant) is called .....
- Concentration of the radioactive element after one average life is ..... of the original concentration.
- $^{24}_{11}\text{Na} \xrightarrow{(p, n)} ^{24}_{12}\text{Mg}$  reaction is written as .....

- Nuclear reaction  $^{14}_7\text{N} + ^4_2\text{He} \longrightarrow ^{17}_8\text{O} + ^1_1\text{H}$  is written as .....
- There should be a ..... of the fissionable material to maintain a fission chain.
- Graphite is used in the nuclear reactor as a .....
- IUPAC representation of the element of atomic number 115 is .....
- The overall reaction in the sun responsible for the energy it radiates is .....
- Elements with atomic numbers greater than 92 are called the ..... elements.
- The more ..... the packing fraction of an element, the more stable should be the nucleus.
- Energy equivalent of 1 amu is ..... MeV.
- Age of dead bodies is determined by .....
- Cobalt-60 used in the treatment of .....
- ..... is a device that detects nuclear radiations from flashes of light generated in a matter by the radiation.
- A REM is a unit of ..... used to relate various kinds of radiation in terms of biological destruction.
- Unit of radioactive disintegration constant is .....
- Element formed from  $^{238}_{92}\text{U}$  (group IIIB) by emission of 1  $\alpha$ -particle is placed in group .....

### Matrix-Match Type Questions

#### I. Only One Correct

- Match the atomic number of the transuranium element (in List I) with their IUPAC representation in (List II).

| List I | List II |
|--------|---------|
| A. 100 | 1. Unp  |
| B. 101 | 2. Unh  |
| C. 102 | 3. Unq  |
| D. 103 | 4. Unt  |
| E. 106 | 5. Unu  |
|        | 6. Unb  |
|        | 7. Unn  |

- Match the name of scientist (in List I) with the discovery or law (in List II).

| List I                 | List II                       |
|------------------------|-------------------------------|
| A. Henry-Becquerel     | 1. Artificial radioactivity   |
| B. Soddy-Fajan         | 2. Cyclotron                  |
| C. Rutherford          | 3. Group displacement law     |
| D. I. Curie, F. Joliot | 4. Radioactive disintegration |
| E. E.O. Lawrence       | 5. Radioactivity              |

3. Match the series (in List I) with the end product (in List II).

| List I        | List II                   |
|---------------|---------------------------|
| A. $4n$       | 1. $^{207}_{82}\text{Pb}$ |
| B. $(4n + 1)$ | 2. $^{212}_{83}\text{Bi}$ |
| C. $(4n + 2)$ | 3. $^{209}_{83}\text{Bi}$ |
| D. $(4n + 3)$ | 4. $^{206}_{82}\text{Pb}$ |
|               | 5. $^{208}_{82}\text{Pb}$ |
|               | 6. $^{207}_{83}\text{Bi}$ |

4. Match the series (in List I) with starting element (in List II) and end element (in List III).

| List I        | List II                   | List III                    |
|---------------|---------------------------|-----------------------------|
| A. $4n$       | 1. $^{241}_{94}\text{Pu}$ | I. $^{207}_{87}\text{Pb}$   |
| B. $(4n + 1)$ | 2. $^{232}_{92}\text{Th}$ | II. $^{209}_{83}\text{Bi}$  |
| C. $(4n + 2)$ | 3. $^{235}_{92}\text{U}$  | III. $^{209}_{83}\text{Pb}$ |
| D. $(4n + 3)$ | 4. $^{238}_{92}\text{U}$  | IV. $^{206}_{82}\text{Pb}$  |

## II. One or More Correct

1. Match the Column I with the properties (one or more) in Column.

| Column I                        | Column II                                                     |
|---------------------------------|---------------------------------------------------------------|
| A. Determination of age of rock | 1. $N = N_0 \left(\frac{1}{2}\right)^y$                       |
| B. Carbon-dating                | 2. $\frac{0.693}{\lambda}$                                    |
| C. Half-life                    | 3. $^{238}_{92}\text{U} \longrightarrow ^{206}_{82}\text{Pb}$ |
| D. $\alpha$ -particle           | 4. $^{14}_6\text{C} \longrightarrow ^{14}_7\text{N}$          |
| E. $\beta$ -particle            | 5                                                             |

2. Match the Column I giving particles with the reaction involving these particles (on or more) in Column II.

| Column I           | Column II                                                    |
|--------------------|--------------------------------------------------------------|
| A. $^4_2\text{He}$ | 1. $^{14}_7\text{N} \longrightarrow ^{17}_8\text{O}$         |
| B. $^1_1\text{H}$  | 2. $^{27}_{13}\text{Al} \longrightarrow ^{30}_{15}\text{P}$  |
| C. $^1_0n$         | 3. $^{30}_{15}\text{P} \longrightarrow ^{30}_{14}\text{Si}$  |
| D. $^0_{-1}e$      | 4. $^{23}_{11}\text{Na} \longrightarrow ^{24}_{11}\text{Na}$ |
| E. $^0_1e$         | 5. $^{24}_{11}\text{Na} \longrightarrow ^{24}_{12}\text{Mg}$ |

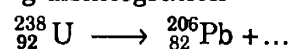
## Integer Answer Types

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the ORS have to be darkened. For example, if the correct answers to question number X, Y, Z and W (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will like the following :

| X                       | Y                       | Z                       | W                       |
|-------------------------|-------------------------|-------------------------|-------------------------|
| <input type="radio"/> 0 | <input type="radio"/> 0 | <input type="radio"/> 0 | <input type="radio"/> 0 |
| <input type="radio"/> 1 | <input type="radio"/> 1 | <input type="radio"/> 1 | <input type="radio"/> 1 |
| <input type="radio"/> 2 | <input type="radio"/> 2 | <input type="radio"/> 2 | <input type="radio"/> 2 |
| <input type="radio"/> 3 | <input type="radio"/> 3 | <input type="radio"/> 3 | <input type="radio"/> 3 |
| <input type="radio"/> 4 | <input type="radio"/> 4 | <input type="radio"/> 4 | <input type="radio"/> 4 |
| <input type="radio"/> 5 | <input type="radio"/> 5 | <input type="radio"/> 5 | <input type="radio"/> 5 |
| <input type="radio"/> 6 | <input type="radio"/> 6 | <input type="radio"/> 6 | <input type="radio"/> 6 |
| <input type="radio"/> 7 | <input type="radio"/> 7 | <input type="radio"/> 7 | <input type="radio"/> 7 |
| <input type="radio"/> 8 | <input type="radio"/> 8 | <input type="radio"/> 8 | <input type="radio"/> 8 |
| <input type="radio"/> 9 | <input type="radio"/> 9 | <input type="radio"/> 9 | <input type="radio"/> 9 |

## Set I

1. In the following disintegration



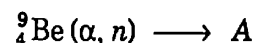
number of  $\beta$ -particles emitted is .....

2. In question (1) above, number of  $\alpha$ -particles emitted is .....
3. 16 g X changes to 1 g (half life 1 day) after ..... days
4. Atomic number of positron is taken as .....
5. When  $^7_4\text{Be}$  captures one electron, mass number of the element formed is .....
6. Charge on  $\alpha$ -particles is  $X^+$ ; X is .....
7. Charge of  $\gamma$ -particles is .....
8. 10 g of a radioactive element loses 8.75 g in 9 days. Thus, half-life is ..... days.

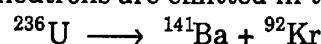
## Set II

1. 1.00 mL solution containing 0.24  $\mu\text{Ci}$  of tritium is injected into a dog's blood stream. After a period of time to allow the isotope to be dispersed, a 1.00 mL sample of blood is drawn. The radioactivity of this sample is found to be 0.04  $\mu\text{Ci/mL}$ . What is the total volume of blood in the dog?

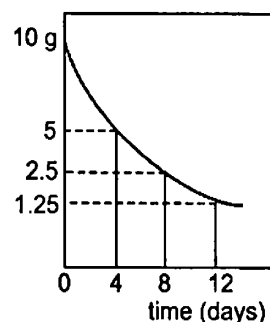
2. How many neutrons are contained in A formed by the reaction?



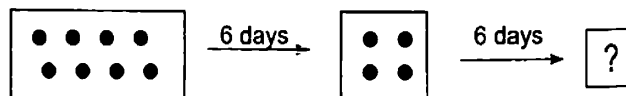
3. How many neutrons are emitted in the reaction?



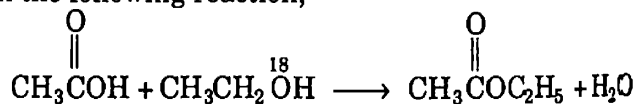
4. In the following decay process, half-life is ..... days



5. What is the number of particles left in the following decay process?



6. In the following reaction,



molar mass difference between water formed in the reaction and ordinary water is ..... unit.

7. How many curies are contained in the radioactive change with activity  $18.5 \times 10^{10}$  dps?
8. Carbon-dating uses carbon isotope with number of neutrons .....

# Answers & Solutions

## Master Exercises

### Exercise 1

#### Analytical Questions

1. Half-life = 4.8 min

(a) time = 19.2 min

$$y = \text{number of half-life} = \frac{19.2}{4.8} = 4$$

$$\begin{aligned} C &= C_0 \left(\frac{1}{2}\right)^y \\ &= 1 \text{ mg} \left(\frac{1}{2}\right)^4 \\ &= \frac{1}{16} \text{ mg} \\ &= 0.0625 \text{ mg} \end{aligned}$$

(b)

time = 48 min

$$y = \frac{48}{4.8} = 10$$

time of 99.9% reaction = 10 times of half-life

hence, 99.9% reacted

$$\begin{aligned} \text{unreacted} &= 0.1\% = 1 \times \frac{0.1}{100} \\ &= 1 \times 10^{-3} \text{ mg} \end{aligned}$$

$$2. -\frac{dN}{dt} = \lambda N$$

$$0.1 \text{ mg } ^{239}\text{Pu} = 0.1 \times 10^{-3} \text{ g} = \frac{0.1 \times 10^{-3}}{239} \text{ mol}$$

$$N = \frac{0.1 \times 10^{-3} \times 6.02 \times 10^{23}}{239} \text{ atoms}$$

$$1.4 \times 10^7 = \frac{\lambda \times 0.1 \times 10^{-3} \times 6.02 \times 10^{23}}{239}$$

$$\lambda = 5.56 \times 10^{-11} \text{ min}^{-1}$$

$$t_{50} = \frac{0.693}{\lambda} = 7.481 \times 10^{11} \text{ s}$$

$$= 2.372 \text{ years}$$

$$\lambda = \frac{2.303}{t} \log \frac{C_0}{C}$$

$$t = \frac{2.303}{\lambda} \log \frac{C_0}{C}$$

$$= \frac{2.303 \times t_{50}}{0.693} \log \left(\frac{C_0}{C}\right)$$

$$(a) \quad t = \frac{2.303 \times 14.8}{0.693} \log \frac{100}{10}$$

$$= 49.184 \text{ h}$$

$$(b) \quad t = \frac{2.303 \times 14.8}{0.693} \log \frac{100}{5} = 64 \text{ h}$$

4.

$$N_1 \lambda_1 = N_2 \lambda_2$$

radium uranium

$$\frac{\lambda_1}{\lambda_2} = \frac{N_2}{N_1} = \frac{28}{1}$$

$$\frac{\left(\frac{0.693}{t_{50}}\right)_1}{\left(\frac{0.693}{t_{50}}\right)_2} = \frac{(t_{50})_2}{(t_{50})_1} = \frac{28}{1}$$

$$(t_{50})_2 = 1620 \times 28 \text{ years} = 1.43047 \times 10^{12} \text{ s}$$

$$\therefore \lambda_2 = \frac{0.693}{t_{50}} = 4.844 \times 10^{-13} \text{ s}^{-1}$$

5.

$$1 \text{ g radium} = \frac{N_0}{226} \text{ atoms}$$

$$-\frac{dN}{dt} = \frac{\lambda N_0}{226}$$

$$11.6 \times 10^{17} = \frac{4.353 \times 10^{-4} N_0}{226}$$

$$\therefore N_0 = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$6. \quad 1 \text{ mCi} = 0.001 \text{ Ci} = 3.7 \times 10^7 \text{ dps}$$

$$t_{50} = 5720 \text{ years}$$

$$= 5720 \times 3.1536 \times 10^7 \text{ s}$$

$$(1 \text{ yr} = 3.1536 \times 10^7 \text{ s})$$

$$\lambda = \frac{0.693}{t_{50}} = \frac{0.693}{5720 \times 3.1336 \times 10^7} \text{ s}^{-1}$$

$$\frac{dN}{dt} = \lambda \left(\frac{w}{14}\right) \times 6.02 \times 10^{23} \text{ atom s}^{-1}$$

$$3.7 \times 10^7 = \frac{0.693}{3.1536 \times 10^7 \times 5720} \times \frac{w \times 6.02 \times 10^{23}}{14}$$

$$w = 2.24 \times 10^{-4} \text{ g}$$

7.

$$1.00 \mu\text{Ci} = 1.0 \times 10^{-6} \text{ Ci}$$

$$= 3.7 \times 10^{10} \times 1.0 \times 10^{-6} \text{ dps}$$

$$\therefore -\frac{dN}{dt} = 3.7 \times 10^4 \text{ dps}$$

$$1 \text{ year} = 3.1536 \times 10^7 \text{ s}$$

$$\lambda = \frac{0.693}{t_{50}} = \frac{0.693}{1.28 \times 10^9 \times 3.1536 \times 10^7}$$

$$= 1.72 \times 10^{-17} \text{ s}^{-1}$$

$$-\frac{dN}{dt} = \lambda N = \frac{\lambda w N_0}{40}$$

$$3.7 \times 10^4 = \frac{1.72 \times 10^{-17} \times w \times 6.02 \times 10^{23}}{40}$$

$$8. \quad w = 0.143 \text{ g}$$

$${}_{84}^{210}\text{Po} \longrightarrow {}_2^4\text{He} + {}_{82}^{206}\text{Pb}$$

$$1 \text{ g Po} = \frac{1}{210} \text{ mol Po}$$

$$\text{Po left in 69.2 days} = C = C_0 \left(\frac{1}{2}\right)^y$$

$$\text{where, } y = \frac{\text{total time}}{t_{50}} = \frac{69.2}{138.4} = \left(\frac{1}{2}\right)$$

$$C = 1 \left(\frac{1}{2}\right)^{1/2}$$

$$= 0.7071 \text{ g}$$

$$\text{Po changed to helium} = 1 - 0.7071 \text{ g}$$

$$= 0.2929 \text{ g}$$

$$= 1.3947 \times 10^{-3} \text{ mol}$$

$$\text{Helium formed} = 31.24 \text{ cc at STP}$$

$$9. \text{ Initial amount of an } \alpha\text{-active isotope} = N_0 = 10 \text{ g atom}$$

$$\text{Helium formed} = 11.2 \text{ cc at STP}$$

$$= \frac{11.2}{22400} \text{ g atom at STP}$$

$$= 5 \times 10^{-4} \text{ g atom}$$

$$\therefore \text{Element left} = (10 - 5 \times 10^{-4})$$

$$= 9.9995 \text{ g atom}$$

$$\lambda = \frac{2.303}{t} \log \frac{N_0}{N}$$

$$= 2.303 \log \frac{10}{9.9995} = 5 \times 10^{-5} \text{ h}^{-1}$$

$$t_{50} = \frac{0.693}{\lambda} = \frac{0.693}{5 \times 10^{-5}} \text{ h}$$

$$= 13857 \text{ h} = 1.582 \text{ years}$$

$$10. \text{ Amount left after 10 days} = \text{amount disintegrating on 11th day.}$$

$$C = C_0 \left(\frac{1}{2}\right)^y \quad y = \frac{\text{total time}}{t_{50}} = 2$$

$$= 0.1 \left(\frac{1}{2}\right)^2$$

$$= 0.1 \times \frac{1}{4}$$

$$= 0.025 \text{ g atm after 10 days}$$

$$\text{Amount left on 11th day} \left( y = \frac{1}{5} \text{ half-life} \right)$$

$$\text{when } C_0 = 0.025 \text{ g atom}$$

$$C = 0.025 \left(\frac{1}{2}\right)^{1/5} \text{ g atom}$$

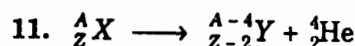
$$= 0.0218 \text{ g atom}$$

$$\text{Amount disintegrating on 11th day} = C_0 - C$$

$$= 0.025 - 0.0218$$

$$= 3.2 \times 10^{-3} \text{ g atom}$$

$$= 1.926 \times 10^{21} \text{ atom}$$



$$t_{50} = 10 \text{ days}$$

$$\therefore y = \frac{t}{t_{50}} = \frac{20}{10} = 2$$

X left after 20 days

$$C = C_0 \left(\frac{1}{2}\right)^y = \frac{1}{4} \text{ g atom}$$

$\therefore$  Helium formed = amount of X decomposed

$$= 1 - \frac{1}{4} = \frac{3}{4} \text{ mol}$$

$$\therefore \text{Volume at STP} = \frac{3}{4} \times 22.4 \text{ L}$$

$$= 16.8 \text{ L}$$

$$12. \quad -\frac{dN}{dt} = \lambda N_0 \text{ at start}$$

$$-\frac{dN}{dt} = \lambda N \text{ after time } t$$

$$4750 = \lambda N_0$$

$$2700 = \lambda N$$

$$\therefore \frac{N_0}{N} = \frac{4750}{2700}$$

$$\text{Also } \lambda = \frac{2.303}{t} \log \frac{N_0}{N}$$

$$= \frac{2.303}{5} \log \frac{4750}{200} = 0.113 \text{ min}^{-1}$$

$$\therefore t_{50} = \frac{0.693}{\lambda} = \frac{0.693}{0.113} = 6.1328 \text{ min}$$

$$13. \text{ Let initial amount} = 10 = N_0$$

$$\text{Amount decomposed} = 99.99\%$$

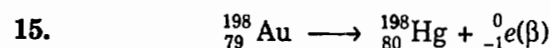
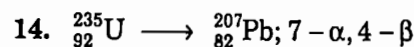
$$N = \text{amount left} = 100 - 99.99$$

$$= 0.01$$

$$\therefore \lambda = \frac{2.303}{t} \log \frac{N_0}{N}$$

$$\frac{0.693}{1.53} = \frac{2.303}{t} \log \frac{100}{0.01}$$

$$t = 20.34 \text{ s}$$



Au and Hg are isobars.

$$\text{Half-life} = 65 \text{ days, } t = 260 \text{ days}$$

$$y = \frac{\text{total time}}{\text{half-life}} = 4$$

Au left

$$C = C_0 \left(\frac{1}{2}\right)^y = 1 \left(\frac{1}{2}\right)^4 = \frac{1}{16} \text{ g}$$

$$\text{Hg formed} = C_0 - C = 1 - \frac{1}{16} = \frac{15}{16} = 0.9375 \text{ g}$$

$$16. \quad \left[ 1 + \frac{[\text{Pb}]}{[\text{U}]} \right] = 1 + \left( \frac{0.1}{\frac{206}{1}} \right) = 1.1155 = (2)^y$$

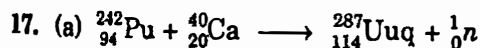
$$y = \frac{t}{t_{50}}$$

$$y \log 2 = \log 1.1155$$

$$y = 0.1578$$

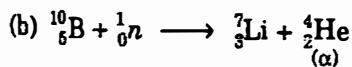
$$t = 4.5 \times 10^9 \times 0.1578$$

$$= 7.1 \times 10^8 \text{ years}$$



Uuq has atomic number 114

$\uparrow \uparrow \uparrow$   
1 1 4



19.  $\Delta E = 4.795 - 4.611 = 0.184 \text{ MeV}$

$$= 0.184 \times 10^6 \text{ eV}$$

$$= 0.184 \times 10^6 \times 1.6 \times 10^{-19} \text{ J}$$

$$= 2.944 \times 10^{-14} \text{ J}$$

$$\Delta E = \frac{hc}{\lambda}$$

$$\therefore \lambda = \frac{hc}{\Delta E} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{2.944 \times 10^{-14}}$$

$$= 6.746 \times 10^{-12} \text{ m}$$

$$= 6.746 \text{ pm}$$

20. 827.5 nm

|         | Mass defect<br>g mol <sup>-1</sup> | BE<br>MeV/neutron |
|---------|------------------------------------|-------------------|
| 21. (a) | 0.467                              | 8.72              |
| (b)     | 0.60015                            | 8.76              |

22. Refer Q. 22.

23.  $\left(1 + \frac{[\text{Pb}]}{[\text{U}]}\right) = 2^y$

$$\left(1 + \frac{20.6/206}{23.8/238}\right) = 2^y$$

$$2 = 2^y$$

$$y = 1$$

$$\frac{t}{t_{50}} = 1$$

$$t = 4.5 \times 10^9 \text{ years}$$

2. Mass defect =  $15.995 - [8(1.0073 + 1.0087 + 0.000548)]$

$$= 15.995 - 16.132384 = 0.137384 \text{ unit}$$

$$\therefore \text{BE} = 0.137384 \times 931 \text{ MeV}$$

$$= 127.9045 \text{ MeV}$$

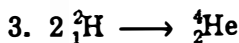
$$= 127.9045 \times 10^6 \text{ eV}$$

$$= 127.9045 \times 10^8 \times 1.6 \times 10^{-19} \text{ J}$$

$$= 2.046 \times 10^{-11} \text{ J per molecule}$$

$$= 2.046 \times 10^{-11} \times 6.02 \times 10^{23}$$

$$= 1.232 \times 10^{13} \text{ J mol}^{-1}$$



$$\text{Mass defect} = m({}_2^4\text{He}) - 2m({}_1^2\text{H})$$

$$= 4.0026 - 2 \times 2.0141$$

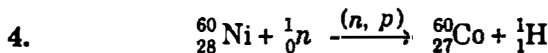
$$= -0.0256 \text{ units}$$

$$= -0.0256 \times 10^{-3} \text{ kg unit}$$

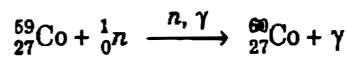
$$\therefore \text{BE} = \Delta mc^2$$

$$= 0.0256 \times 10^{-3} \times (2.998 \times 10^8)^2$$

$$= 2.3 \times 10^{12} \text{ J}$$



Target nucleus  ${}_{28}^{60}\text{Ni}$



Target nucleus =  ${}_{27}^{60}\text{Co}$

Half-life of  ${}_{27}^{60}\text{Co}$  = 7 years

$$t_{50} = 7 \times 3.1536 \times 10^7 \text{ s}$$

$$\therefore \lambda = \frac{0.693}{t_{50}} = \frac{0.693}{7 \times 3.1536 \times 10^7} \text{ s}^{-1}$$

$$= 3.14 \times 10^{-9} \text{ s}^{-1}$$

5.

$$\lambda = \frac{2.303}{t} \log \frac{C_0}{C}$$

$$\frac{0.693}{t_{50}} = \frac{2.303}{t} \log \frac{C_0}{C}$$

$$\frac{0.693}{5770} = \frac{2.303}{t} \log \frac{100}{60}$$

$$t = 4254 \text{ years}$$

6.

$$-\frac{dN}{dt} = \lambda N$$

$$3.7 \times 10^{10} = \frac{0.693 \times w \times 6.02 \times 10^{23}}{40 \times 60 \times 60 \times 140}$$

$$\therefore w = 1.8 \times 10^{-6} \text{ g}$$

7. Refer text.

## NCERT Problems

1. Mass defect

$$= 7.016 - (4 \times 1.008665 + 3 \times 1.007277 + 3 \times 0.000548)$$

$$= 7.016 - 7.058135$$

$$= -0.042135 \text{ units}$$

$$\therefore \text{BE} = 0.042135 \times 931 \text{ MeV} = 39.228 \text{ MeV}$$

$$\therefore \text{BE per nucleon} = \left(\frac{\text{BE}}{7}\right) = 5.604 \text{ MeV/nucleon}$$



## Exercise 2

### Only One Option Correct

1. In the chain reaction,

|             | Energy     | Neutrons |
|-------------|------------|----------|
| 1st step    | $E$        | 3        |
| 2nd step    | $3E$       | 9        |
| 3rd step    | $9E$       | 27       |
| $n$ th step | $3^{n-1}E$ | $3^n$    |

Thus, (d)

2. (d) 3. (d) 4. (a) 5. (c) 6. (c) 7. (b)

8. (d) 9. (c) 10. (a) 11. (c) 12. (d) 13. (a)

14. (b)

15. To determine age by rock-dating

$$1 + \frac{[\text{Pb}]}{[\text{U}]} = 2^y$$

$$(1 + 1) = (2)^y$$

$$\therefore y = 1$$

$$\therefore \frac{t}{T_{50}} = y = 1$$

$$\therefore t = T_{50} = 4.5 \times 10^9 \text{ year}$$

Thus, (b)

16. Disintegration constant  $k = 0.49 \times 10^{-10} \text{ year}^{-1}$

$$\therefore T_{50} = \frac{0.693}{k} = \frac{0.693}{0.49 \times 10^{-10} \text{ year}^{-1}}$$

$$= 1.41 \times 10^{10} \text{ year}$$

Thus, (c)

17. Mass defect = 0.02 amu

$$= \frac{0.02}{N_0} \text{ g atom}^{-1}$$

$$= \frac{0.02}{N_0} \times N_0 \text{ g mol}^{-1}$$

$$= 0.02 \text{ g mol}^{-1}$$

$$E = mc^2 = 0.02 \times 9 \times 10^{20} \text{ erg mol}^{-1}$$

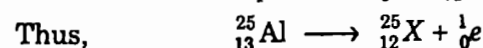
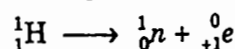
$$= \frac{0.02 \times 9 \times 10^{20} \times 0.002}{8.314 \times 10^7 \times 10^6} \text{ million kcal mol}^{-1}$$

$$\approx 430 \quad \left( \begin{array}{l} 1 \text{ million} = 10^6 \\ 8.314 \times 10^7 \text{ erg} = 0.002 \text{ kcal} \end{array} \right)$$

Thus, (a)

18. (d) 19. (c)

20. Positron is emitted with proton changes to neutron



Number of electrons remained = 13 (as in Al)

Thus, (a)  ${}^{25}_{12}\text{X}$  has 12p, 13n, 13e.

21. (c)

22.

$$C = C_0 \left( \frac{1}{2} \right)^y$$

$$(3.00 \times 10^8) = (2.40 \times 10^9) \left( \frac{1}{2} \right)^y$$

$$\left( \frac{1}{2} \right)^y = \left( \frac{1}{8} \right) = \left( \frac{1}{2} \right)^3$$

$$\therefore y = 3$$

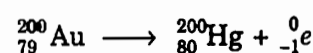
$$\text{or } \frac{t}{T_{50}} = 3$$

$$\therefore t = 3 \times T_{50} = 36.78 \text{ years}$$

Thus, (d)

23. (c)

24.  $\beta$ -particle emission gives isobar.



$$C = C_0 \left( \frac{1}{2} \right)^y$$

$$y = \frac{52}{13} = 4$$

$$C = 1 \left( \frac{1}{2} \right)^4 = \frac{1}{16}$$

$$\therefore \text{Au left} = \frac{1}{16} \text{ g}$$

$$\text{Au changed to Hg} = 1 - \frac{1}{16} = \frac{15}{16} = 0.9375 \text{ g}$$

Thus, (b)

$$25. \quad \frac{N_A}{N_B} = \frac{(T_{50})_A}{(T_{50})_B}$$

$$3.1 \times 10^9 = \frac{2 \times 10^{10}}{(T_{50})_B}$$

$$(T_{50})_B = 6.45 \text{ year}$$

Thus, (b)

$$26. \quad -\frac{dN}{dt} = kN = k \frac{w}{A} N_0$$

$$3.7 \times 10^{10} = 4.4 \times 10^{-12} \times \frac{w}{14} \times 6.02 \times 10^{23}$$

$$w = 2 \times 10^{-4} \text{ kg} \quad (1 \text{ Ci} = 3.7 \times 10^{10} \text{ dps})$$

Thus, (a)

27. (c)

$$28. \quad [\text{Pb}] = \frac{0.618 \times 10^{-6}}{206} \text{ mol} = 3 \times 10^{-9} \text{ mol}$$

$$[\text{U}] = \frac{0.238 \times 10^{-6}}{238} \text{ mol} = 1 \times 10^{-9} \text{ mol}$$

$$\text{For rock-dating, } \left( 1 + \frac{[\text{Pb}]}{[\text{U}]} \right) = (2)^y$$

$$\therefore y = 2 = \frac{t}{T_{50}}$$

$$\therefore t = 3.0 \times 10^9 \text{ years}$$

Thus, (b)

29.  $T_A = \frac{0.693}{k_A}$  by first order rate law (based on unit of  $k_A$ )

$T_B = \frac{1}{k_B a}$  by second order rate law (based on unit of  $k_B$ )

$$\therefore \frac{T_A}{k_A} = \frac{T_B}{k_B a} \quad (\text{given})$$

$$\therefore \frac{k_A}{k_B} = 0.693 a$$

$$(\text{Rate})_A = k_A(a)$$

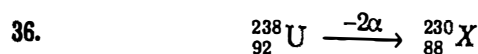
$$(\text{Rate})_B = k_B(a)^2$$

$$\therefore \frac{(\text{Rate})_A}{(\text{Rate})_B} = \frac{k_A}{k_B a} = 0.693 = k_A T_A$$

Thus, (c)

30. (c) 31. (d) 32. (b) 33. (a) 34. (a)

35. (c)



Element of atomic number 88 belongs to IIA

Thus, (c)

37. (c) 38. (c) 39. (a) 40. (b) 41. (b)

42. (c) 43. (c) 44. (a) 45. (b) 46. (c)

47. (d) 48. (d) 49. (c) 50. (c)

### One or More Than One Options Correct

1. (c) 2. (a),(b),(d) 3. (a) 4. (b),(c),(d)

5. (a),(b),(d) 6. (a),(b),(c) 7. (b),(d) 8. (a),(b),(d)

9. (c),(d) 10. (a),(b),(c)

### Brain Twisters

1.  $\lambda = \frac{2.303}{t} \log \frac{100}{5}$

$$\frac{0.693}{t_{50}} = \frac{2.303}{t} \log 20$$

$$\therefore \frac{0.693}{2.62} = \frac{2.303}{t} \log 20$$

$$t = 11.33 \text{ years}$$

2.  $1 \text{ g radium} = \frac{N_0}{226} \text{ atoms}$

$$-\frac{dN}{dt} = \frac{\lambda N_0}{226}$$

$$11.6 \times 10^{17} = \frac{4.353 \times 10^{-4} N_0}{226}$$

$$\therefore N_0 = 6.02 \times 10^{23} \text{ mol}^{-1}$$

3.  $t_{50} = 28.1 \text{ years}$

$$\lambda = \frac{2.303}{t} \log \frac{C_0}{C}$$

$$\frac{0.693}{t_{50}} = \frac{2.303}{t} \log \frac{C_0}{C}$$

$$\frac{0.693}{28.1} = \frac{2.303}{20} \log \frac{1 \times 10^{-6}}{C}$$

$$C = 0.6107 \times 10^{-6} \text{ g}$$

$$= 0.6107 \mu\text{g}$$

4.  $2.8 \text{ nCi} = 2.8 \times 10^{-9} \text{ Ci}$

$$= 2.8 \times 10^{-9} \times 3.7 \times 10^{10} \text{ dps}$$

$$= 103.6 \text{ dps}$$

$$103.6 = -\frac{dN}{dt} = \lambda \times \frac{30 \times 10^{-6} \times 6.02 \times 10^{23}}{247}$$

$$\lambda = 1.417 \times 10^{-15} \text{ s}^{-1}$$

$$\therefore t_{50} = \frac{0.693}{\lambda} = 4.891 \times 10^{14} \text{ s}$$

$$= 1.551 \times 10^7 \text{ years}$$

5.  $\lambda = \frac{0.693}{t_{50}} = \frac{0.693}{0.5} \text{ h}^{-1}$

$$-\frac{dN}{dt} = \lambda N$$

$$-\frac{dN}{dt} = 10 \text{ dis min}^{-1} = 10 \times 60 \text{ dis h}^{-1}$$

$$10 \times 60 = \frac{0.693}{0.5} N$$

$$N = 207.9 \text{ atoms}$$

6.  $1 \text{ Ci} = 3.7 \times 10^{10} \text{ dps}$

$$t_{50} = 5730 \text{ years} = 5730 \times 3.1536 \times 10^7 \text{ s}$$

$$\therefore \lambda = \frac{0.693}{t_{50}} = \frac{0.693}{5730 \times 3.1536 \times 10^7} \text{ s}^{-1}$$

$$-\frac{dN}{dt} = \lambda N = \frac{\lambda w \times 6.02 \times 10^{23}}{14}$$

$$3.7 \times 10^{10} = \frac{0.693 \times w \times 6.02 \times 10^{23}}{5730 \times 3.1536 \times 10^7 \times 14}$$

$$w = 0.2244 \text{ g}$$

7.  $8.27 \times 10^{-4} \text{ nm}$

8. Refer solved example 5.21

9.  $\text{Energy} = 200 \text{ kWh} = 200 \times 10^3 \text{ watt}$

$$= 200 \times 10^3 \text{ J s}^{-1}$$

$$= 200 \times 10^3 \times 3600 \text{ J h}^{-1}$$

$$= \frac{200 \times 10^3 \times 3600}{1.6 \times 10^{-19}} \text{ eV}$$

$$= 4.5 \times 10^{27} \text{ eV}$$

$$\text{Molecules of H}_2 \text{ produced} = \frac{4.5 \times 10^{27} \times 1.7}{100}$$

$$= 7.65 \times 10^{25} \text{ molecules}$$

$$= \frac{7.65 \times 10^{25}}{6.02 \times 10^{23}} \text{ mol H}_2$$

$$= 127.076 \text{ mol H}_2$$

$$= 2846.5 \text{ L at STP}$$

10. Mass defect = 49.9516 - 49.94479  
 $= 6.81 \times 10^{-3} \text{ amu}$   
 Binding energy =  $6.81 \times 10^{-3} \times 931 \text{ MeV}$   
 $= 6.34011 \text{ MeV}$   
 Kinetic energy of the emitted  $\beta^-$  particle = 0.80 V  
 $\therefore$  Kinetic energy of neutrino emitted = 5.54 MeV

11.  ${}^{14}_6\text{C} \longrightarrow {}^{14}_7\text{N} + {}^0_{-1}e$   
 Mass defect =  ${}^{14}_6\text{C} - {}^{14}_7\text{N} = 14.00324 - 14.00307$   
 $= 1.7 \times 10^{-4} \text{ amu}$   
 Binding energy =  $1.7 \times 10^{-4} \times 931 \text{ MeV}$   
 $= 0.1583 \text{ MeV per nucleon}$   
 $1 \text{ Ci} = 3.7 \times 10^{10} \text{ dps}$   
 $= 3.7 \times 10^{10} \times 3600 \text{ dph}$   
 $\therefore$  Total heat =  $3.7 \times 10^{10} \times 3600 \times 0.1583 \text{ MeV}$   
 $= 2.1086 \times 10^{13} \text{ MeV}$   
 $= 2.1086 \times 10^{19} \text{ eV}$   
 $= 2.1086 \times 10^{19} \times 1.6 \times 10^{-19} \text{ J}$

12.  $\frac{[\text{Pb}]}{[\text{Th}]} = \left( \frac{0.2}{208} \times 232 \right) = 0.2231$

$\therefore (2)^y = 1 + \frac{[\text{Pb}]}{[\text{Th}]} = 1.2231$

$\therefore y \log 2 = 0.08745$

$y = 0.2905$

$\frac{t}{t_{50}} = 0.2905$

$\therefore t = 0.2905 \times T_{50}$   
 $= 0.2905 \times \frac{0.693}{4.98 \times 10^{-11}}$

$= 4.04 \times 10^9 \text{ years}$

13.  $\lambda = \frac{2.303}{t} \log \frac{C_0}{C}$

$\frac{0.693}{5730} = \frac{2.303}{t} \log \frac{15}{10}$

$\therefore t = 3353 \text{ years}$

14.  $\lambda = \frac{2.303}{t} \log \frac{C_0}{C}$

$\frac{0.693}{5730} = \frac{2.303}{t} \log \frac{15.3}{9.4}$

$t = 4028.62 \text{ year}$

15. (Ar) = 65.9 atoms =  $N_0$

(K) = 39.1 atoms =  $N$

$\therefore \lambda = \frac{2.303}{t} \log \frac{N_0}{N}$

$\frac{0.693}{t_{50}} = \frac{2.303}{t} \log \frac{N_0}{N}$

$\frac{0.693}{1.3 \times 10^9} = \frac{2.303}{t} \log \frac{65.9}{34.1}$

$\therefore t = 1.236 \times 10^9 \text{ years}$

17.  $7.4 \text{ mCi} = 7.4 \times 10^{-3} \text{ Ci} = 7.4 \times 10^{-3} \times 3.7 \times 10^{10} \text{ dps}$   
 $= 2.738 \times 10^8 \text{ dps}$

$\therefore -\frac{dN}{dt} = \lambda N$

$t_{50} = 8.1 \text{ days}$

$= 8.1 \times 24 \times 3600 \text{ s}$

$\lambda = \frac{0.693}{t_{50}}$

$2.738 \times 10^8 = \frac{0.693 N}{8.1 \times 24 \times 3600}$

$N = 2.765 \times 10^{14} \text{ atoms}$

## Passage Comprehension Questions

### Passage 1

1. (c) 2. (a),(b),(c) 3. (a)

### Passage 2

1. (a),(b),(c),(d) 2. (a),(c),(d)

### Passage 3

1. (c) 2. (a)

### Passage 4

1. (b) 2. (c) 3. (d)

### Passage 5

1. (a) 2. (d) 3. (d) 4. (c)

### Passage 6

1. (b) 2. (a) 3. (a)

### Passage 7

1. (a) 2. (b) 3. (c)

### Passage 8

1. (b) 2. (d)

## Assertion & Reason

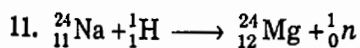
1. (a) 2. (c) 3. (b) 4. (a) 5. (b) 6. (a)

## True & False

1. T 2. T 3. T 4. T 5. T 6. F 7. F  
 8. T 9. F 10. T 11. T 12. F 13. T 14. T  
 15. T 16. F 17. T 18. F 19. T 20. T

## Fill in the Blanks

1. Bq (Becquerel), 1 2. one curie 3. isotope  
 4. conversion of neutron into proton 5. 7, 6  
 6. (a)  ${}^{232}_{90}\text{Th}$ ,  ${}^{208}_{82}\text{Pb}$  (b)  ${}^{241}_{94}\text{Pu}$ ,  ${}^{209}_{83}\text{Bi}$  (c)  ${}^{238}_{92}\text{U}$ ,  ${}^{206}_{82}\text{Pb}$   
 (d)  ${}^{235}_{92}\text{U}$ ,  ${}^{207}_{82}\text{Pb}$   
 7. first 8. irreversible, temperature, pressure

9. average life 10.  $\frac{1}{e}$ 12.  ${}^{14}_7\text{N}(\alpha, p){}^{17}_8\text{O}$  13. critical size 14. moderator15. Uup 16.  $4{}_1^1\text{H} \longrightarrow {}^4_2\text{He} + 2{}_1^0\text{e}(\beta^+)$  17. transuranium

18. negative 19. 931 20. carbon-dating 21. cancer

22. scintillation counter 23. radiation dosage

24.  $\text{time}^{-1}$  25. IIIB**Matrix-Match Type Questions****I. Only One Correct**

- (A)—(7); (B)—(5); (C)—(6); (D)—(4); (E)—(2);
- (A)—(5); (B)—(3); (C)—(4); (D)—(1); (E)—(2);
- (A)—(5); (B)—(3); (C)—(4); (D)—(1);
- (A)—(2)—(III); (B)—(1)—(II); (C)—(4)—(IV); (D)—(3)—(I);

**II. One or More Correct**

- (A)—(1,2,3); (B)—(1,2,4); (C)—(1,2); (D)—(3); (E)—(3,4)
- (A)—(1,2); (B)—(1); (C)—(2,4); (D)—(5); (E)—(3)

**Integer Answer Types****Set I**Questions  $\rightarrow$ Answers  $\rightarrow$ 

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| 6 | 8 | 4 | 1 | 7 | 2 | 0 | 3 |
| ① | ① | ① | ① | ① | ① | ① | ① |
| ① | ① | ① | ① | ① | ① | ① | ① |
| ② | ② | ② | ② | ② | ② | ② | ② |
| ③ | ③ | ③ | ③ | ③ | ③ | ③ | ③ |
| ④ | ④ | ④ | ④ | ④ | ④ | ④ | ④ |
| ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ |
| ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ |
| ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ |
| ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ |
| ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ |

**Set II**Questions  $\rightarrow$ Answers  $\rightarrow$ 

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| 6 | 6 | 3 | 4 | 2 | 0 | 5 | 8 |
| ① | ① | ① | ① | ① | ① | ① | ① |
| ① | ① | ① | ① | ① | ① | ① | ① |
| ② | ② | ② | ② | ② | ② | ② | ② |
| ③ | ③ | ③ | ③ | ③ | ③ | ③ | ③ |
| ④ | ④ | ④ | ④ | ④ | ④ | ④ | ④ |
| ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ |
| ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ |
| ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ |
| ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ |
| ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ |



# 6

**Chemical equations represent a very precise, yet a very versatile, language that describes chemical changes.**

# Chemical Equations and Reactions

## Chemical Equations

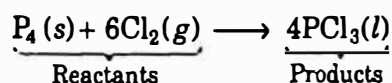
Chemical reactions always involve changing one or more substances into one or more different substances. That is, they involve regrouping atoms or ions to form other substances.

A chemical equation represents the final change in composition when two or more reactants react together to form new substances.

*Thus, chemical equations are used to*

- describe chemical reactions,
- and they show
  - (1) the substances that react, called **reactants**
  - (2) the substances formed, called **products** and
  - (3) the relative amounts of the substances involved.

Take following chemical equation which represents a reaction of stream of chlorine gas,  $\text{Cl}_2$ , with solid phosphorus,  $\text{P}_4$  giving a liquid phosphorus trichloride (which appears as a flame).



In a chemical equation, the formulas for

- the reactants are written to the left of the arrow.
- and that of the products are written to the right of the arrow.
- the physical states of the reactants are also indicated by
  - (s) for solid
  - (l) for liquid
  - (g) for gas

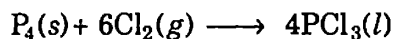
## Learning Framework of the Chapter

- Chemical Equations
- Stoichiometry
- Limiting Reactants
- Yields of Chemical Reactions
- Sequential Reactions

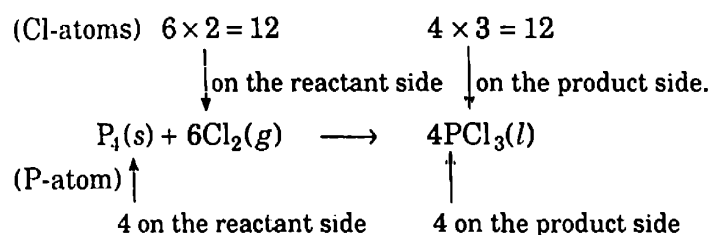
A substance dissolved in water, that is, an aqueous solution of a substance, is indicated by (aq)

Based on the **law of conservation of matter**, which states that **matter can neither be created nor destroyed**, if the total mass of the reactants is 10 g, and if the reaction completely converts the reactants to products, you must end up with 10 g of the products. This also means that if 100 atoms (say) of a particular element are contained in the reactants, then those of 100 atoms must also appear in the products in same fashion.

When we apply law of conservation of matter to the following reaction

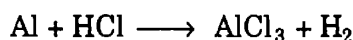


it tells that 1 molecule of phosphorus,  $\text{P}_4$  (with 4 phosphorus atoms) and 6 molecules of diatomic chlorine ( $\text{Cl}_2$ , with 12 chlorine atoms) are required to produce four molecules of  $\text{PCl}_3$ . Because each  $\text{PCl}_3$  molecules contains 1 P atom and 3 Cl atom, hence in all four  $\text{PCl}_3$  molecules are needed.



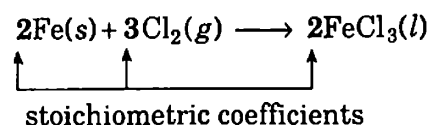
The numbers in front of formulae in balanced chemical equations are required by the law of conservation of matter. The relationship between the quantities of chemical reactants and products is called

**Illustration 1** Al reacts with HCl to form  $\text{AlCl}_3$  and  $\text{H}_2$ . Unbalanced equation is



**Solution** In this form, the equation does not satisfy the Law of conservation of matter as except Al, other atoms are not balanced (Cl one on the left and three on the right, H one on the left and two on the right)

**stoichiometry** and the coefficients in a balanced equation are **stoichiometric coefficients**



This equation is read as :

2 atoms of iron (Fe) combine with 3 molecules of chlorine ( $\text{Cl}_2$ ) to form 2 molecules of ferric chloride ( $\text{FeCl}_3$ )

This equation also represents that 2 moles of iron combine with 3 moles of chlorine ( $\text{Cl}_2$ ) to form 2 moles of  $\text{FeCl}_3$ .

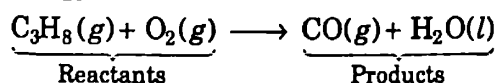
## Balancing the Chemical Equations

Balancing a chemical equation ensures that the same number of atoms of each element appears on both sides of the equation. Many chemical equations can be balanced by trial and error, although some will involve more trial than others when balancing chemical equations,

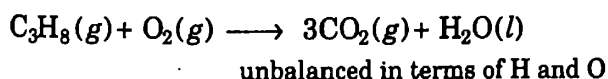
- Formulae for reactants and products must be correct
- Subscripts in the formulae of reactants and products cannot be changed to balance equations. Thus,  $\text{CO}_2$  cannot be changed to CO
- Look for elements that appear in only one place on each side of the equation and balance these elements first.
- If free, uncombined elements appear on either side, balance them last.

| Steps                                                                                                                   | Reaction stage                                                                                                                              | Atoms of<br>Al Cl H<br>Reactants | Al Cl H<br>Products | Conclusion                                           |
|-------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------|---------------------|------------------------------------------------------|
| I Balance Cl by placing 3 before HCl                                                                                    | $\text{Al} + \text{HCl} \longrightarrow \text{AlCl}_3 + \text{H}_2$<br>$\text{Al} + 3\text{HCl} \longrightarrow \text{AlCl}_3 + \text{H}_2$ | 1 1 1<br>1 3 3                   | 1 3 2<br>1 3 2      | Unbalanced chlorine balanced but reaction unbalanced |
| II 3 H appears in LHS and 2 H on RHS. Least common multiple is 6. Multiply HCl on LHS by 2 and $\text{H}_2$ on RHS by 3 | $\text{Al} + 6\text{HCl} \longrightarrow \text{AlCl}_3 + 3\text{H}_2$                                                                       | 1 6 6                            | 1 3 6               | H balanced but reaction is unbalanced                |
| III Balance Cl by multiplying $\text{AlCl}_3$ on RHS by 2                                                               | $\text{Al} + 6\text{HCl} \longrightarrow 2\text{AlCl}_3 + 3\text{H}_2$                                                                      | 1 6 6                            | 2 6 6               | All balanced but Al is not balanced                  |
| IV Balance Al on LHS by multiplying Al on LHS by 2                                                                      | $2\text{Al} + 6\text{HCl} \longrightarrow 2\text{AlCl}_3 + 3\text{H}_2$                                                                     | 2 6 6                            | 2 6 6               | all balanced                                         |
| V Specify physical state                                                                                                | $2\text{Al}(\text{s}) + 6\text{HCl}(\text{aq}) \longrightarrow 2\text{AlCl}_3(\text{aq}) + 3\text{H}_2(\text{g})$                           |                                  |                     |                                                      |

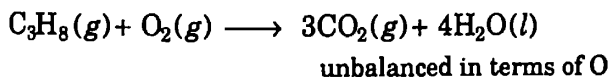
**Illustration 2** We now balance the following reaction with same strategy :



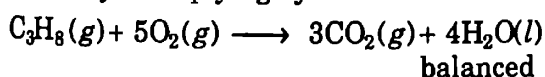
**Solution Step I Balance the C-atoms** Multiply  $\text{CO}_2$  on RHS by 3.



**Step II Balance the H-atoms** Multiply  $\text{H}_2\text{O}$  on RHS by 4



**Step III** There are in all 10 oxygen atoms in RHS Balance O on LHS by multiplying by 5



## Numerical Problem Solving 1

Balance following reactions

- $\text{KClO}_3(\text{s}) \longrightarrow \text{KCl}(\text{s}) + \text{O}_2(\text{g})$
- $\text{P}_4(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{P}_4\text{O}_{10}(\text{s})$
- $\text{Zn}(\text{s}) + \text{HNO}_3(\text{aq}) \longrightarrow \text{Zn}(\text{NO}_3)_2(\text{aq}) + \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- $\text{Al}(\text{s}) + \text{NaOH}(\text{aq}) \longrightarrow \text{NaAlO}_2(\text{aq}) + \text{H}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

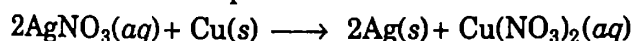
## Different Types of Chemical Reactions

### Reactions in Aqueous Solutions

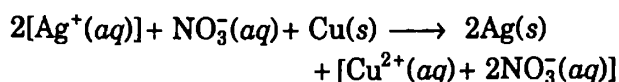
A solution is a homogeneous mixture of two or more substances. One substance is generally considered the solvent, the medium in which another substance-the solute- is dissolved.

There are many important chemical reactions occurring in aqueous solutions where water is the solvent.

- In formula unit equations**, we show complete formulae for all compounds.



- In total ionic equations**, formulae are written to show the (predominant) form in which each substance exists when it is in contact with aqueous solution. Ions that have common source or that remain in solution after the reaction in complete are shown in brackets in total ionic equations



We observe that  $\text{NO}_3^-$  ions do not participate in the reaction. Because they do not change, they are thus simply the "spectator" ions.

- The net ionic equation shows only the species that react. It does not have the spectator ions.

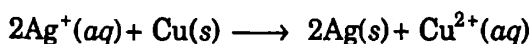
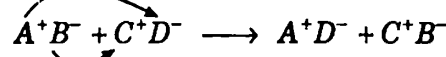
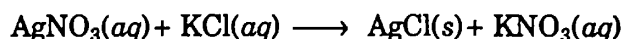


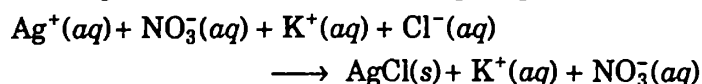
Table 6.1 Can be used to represent a chemical equation in aqueous solution many of the reactions are **exchange reactions** in which the ions of the reactants change partners



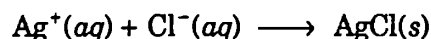
Take the reaction of aqueous silver nitrate with aqueous potassium chloride.



From the table 6.1, we observe  $\text{AgNO}_3$ ,  $\text{KNO}_3$  and  $\text{KCl}$  both are water soluble and thus can give ions in aqueous solution.  $\text{AgCl}$  is insoluble and is thus precipitated.



Net reaction taking place is thus between  $\text{Ag}^+$  and  $\text{Cl}^-$  ion in aqueous solution



## Acid-Base Reactions

- Acid is a substance that gives  $\text{H}^+$  ion in aqueous solution



- Base is a substance that gives  $\text{OH}^-$  ion in aqueous solution



Acid-base reactions are among the most important kinds of chemical reactions.

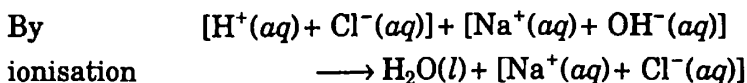
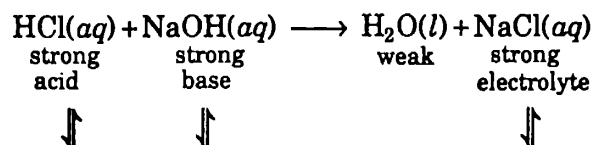
Many acid-base reactions occur in nature in both plants and animals.

The reaction of an acid with a metal hydroxide (base) produces a salt and water. Such reactions are called **neutralisation reactions** due to the fact that acidic and basic properties are lost.

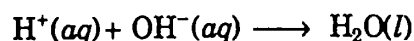
## DEEP Focus

Acid is  $\text{H}^+$  ion donor base is  $\text{OH}^-$  ion donor.

In nearly all neutralisation reactions, the driving force is the combination of  $\text{H}^+(\text{aq})$  from an acid and  $\text{OH}^-(\text{aq})$  from a base to form  $\text{H}_2\text{O}$ .



Cancelling common ion,



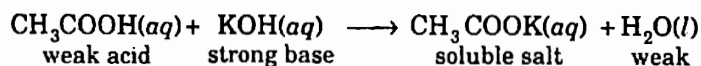
This is the net ionic equation for all reactions of strong acids with strong soluble bases that form soluble salts and water.



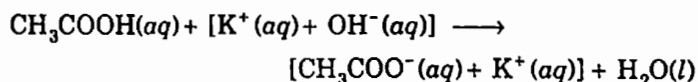
## DEEP Focus

A weak acid is that one that is not ionised completely in aqueous solution. Neutralisation of weak monobasic acid by a strong base results in the formation of soluble salt and  $H_2O$

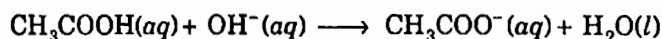
$CH_3COOH$  (acetic acid) is such type one of the weak acids :



Thus, we write



Net reaction is thus :



## Numerical Problem Solving 2

Write net reaction when a weak acid (as  $CH_3COOH$ ) is neutralised by a weak base (as  $NH_4OH$ )

Table 6.1 Solubility of Common Ionic Compounds in Water

| Generally soluble                                                                                         | Exceptions                                                                                                                                                                                                                                                                                                                     |
|-----------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Common inorganic acids (HCl, $H_2SO_4$ , $HNO_3$ , $H_3PO_4$ )                                            | No common exceptions                                                                                                                                                                                                                                                                                                           |
| Low molecular weight organic acid [ $CH_3COOH$ , $HCOOH$ , $(COOH)_2$ ]                                   | No common exceptions                                                                                                                                                                                                                                                                                                           |
| $Na^+$ , $K^+$ , $NH_4^+$ compounds                                                                       | No common exceptions                                                                                                                                                                                                                                                                                                           |
| Chlorides ( $Cl^-$ )                                                                                      | Insoluble, $AgCl$ , $Hg_2Cl_2$ soluble in hot water : $PbCl_2$                                                                                                                                                                                                                                                                 |
| Bromide ( $Br^-$ )                                                                                        | Insoluble : $AgBr$ , $Hg_2Br_2$ , $PbBr_2$<br>Moderately soluble : $HgBr_2$                                                                                                                                                                                                                                                    |
| Iodides ( $I^-$ )                                                                                         | Insoluble : Many heavy metal iodides ( $AgI$ , $PbI_2$ , $CdI_2$ )                                                                                                                                                                                                                                                             |
| Sulphates ( $SO_4^{2-}$ )                                                                                 | Insoluble : $BaSO_4$ , $PbSO_4$ , $HgSO_4$<br>Moderately soluble : $CaSO_4$ , $SrSO_4$ , $Ag_2SO_4$                                                                                                                                                                                                                            |
| Nitrates ( $NO_3^-$ ), Nitrites ( $NO_2^-$ )                                                              | Moderately soluble : $AgNO_2$                                                                                                                                                                                                                                                                                                  |
| Chlorates ( $ClO_3^-$ ), Perchlorates ( $ClO_4^-$ ), Permanganate ( $MnO_4^-$ ), Acetates ( $CH_3COO^-$ ) | Moderately soluble : $CH_3COOAg$                                                                                                                                                                                                                                                                                               |
| Sulphides ( $S^{2-}$ )                                                                                    | Soluble those of $NH_4^+$ , $Na^+$ , $K^+$ , $Mg^{2+}$ , $Ca^{2+}$                                                                                                                                                                                                                                                             |
| Oxides ( $O^{2-}$ ), Hydroxides ( $OH^-$ )                                                                | Soluble : $Li_2O$ , $Na_2O$ , $K_2O$ , $BaO$ (dissolve in $H_2O$ with release of heat i.e., exothermic reactions forming soluble hydroxide $LiOH$ , $NaOH$ , $KOH$ , $Ba(OH)_2$ )<br>Moderately soluble : $CaO$ , $SrO$ (dissolve in $H_2O$ with release of heat, i.e., exothermic reactions forming $Ca(OH)_2$ , $Sr(OH)_2$ ) |

## Generally soluble

## Exceptions

Carbonates ( $CO_3^{2-}$ )  
Phosphate ( $PO_4^{3-}$ )  
Oxalate ( $C_2O_4^{2-}$ )  
Chromate ( $CrO_4^{2-}$ )  
Arsenate ( $AsO_4^{3-}$ )

Soluble : those of  $NH_4^+$ ,  $Na^+$ ,  $K^+$

## Precipitation Reactions

In precipitation reactions an insoluble solid, a **precipitate** forms and then settles out of solution.

## DEEP Focus

The driving force for these reactions is the strong attraction between cations and anions. This results in the removal of ions from solution by the formation of precipitate.

Both silver nitrate and potassium chloride are water-soluble ionic compounds. When combined in water, they undergo an exchange reaction to produce insoluble silver chloride and soluble potassium nitrate



## Reactants

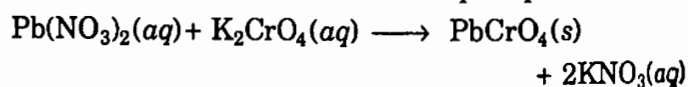
## Products



## Predicting the Outcome of a Precipitation Reaction

Whether the species in the product is precipitated or not, can be predicted by solubility guidelines as given in Table 6.1

$\Rightarrow$  Lead nitrate (soluble) is mixed with potassium chromate (soluble) to form potassium nitrate and lead chromate. In Table 6.1, potassium nitrate is soluble and lead chromate is insoluble and thus is precipitated.

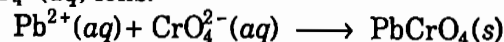


## Reactants

## Products

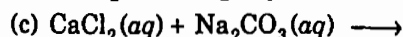
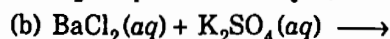
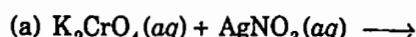


$K^+(aq)$  and  $NO_3^-(aq)$  appear on both sides and thus final outcome is the reaction between  $Pb^{2+}(aq)$  and  $CrO_4^{2-}(aq)$  ions.



## Numerical Problem Solving 3

Write the net ionic reactions of



**Do You Know ---**

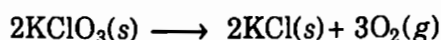
Our teeth and bones were formed by very slow precipitation reactions in which mostly calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$  was deposited in the correct geometric arrangements.

Sea shells, which are formed in a slow precipitation reactions, are mostly calcium carbonate,  $(\text{CaCO}_3)$ , a white compound. Traces of transition metal ions give them colour.

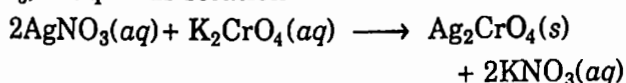
**Stoichiometry**

A basic question raised in the chemical laboratory is, "How much product will be formed from specific amounts of reactants?" Or in some cases, question may be "How much starting material (reactant) must be used to obtain a specific amount of product. **Stoichiometry** (Greek words: *stoicheion* – meaning "first principle or element", and *metron* – meaning "measure") describes the quantitative relationships among element in compounds (**composition stoichiometry**) and among substances as they undergo chemical changes (reaction stoichiometry).

- Two moles of potassium chlorate ( $\text{KClO}_3$ ) on heating (called thermal decomposition) give two moles of potassium chloride ( $\text{KCl}$ ) and three moles of oxygen ( $\text{O}_2$ ) gas

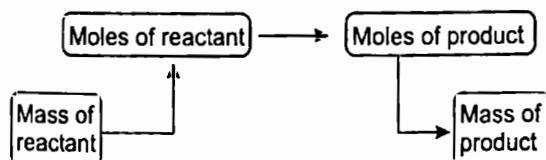


- Two moles silver nitrate ( $\text{AgNO}_3$ ) and one mole potassium chromate ( $\text{K}_2\text{CrO}_4$ ) form one mole silver chromate ( $\text{Ag}_2\text{CrO}_4$ ) and two moles potassium nitrate ( $\text{KNO}_3$ ) is aqueous solution

**Problem Solving Tip**

For stoichiometry

- Write correct formulae for all reactants and products, and balance the resulting equation. A balanced chemical equation must always include the same number of each kind of atom on both sides of the equation.
- Convert the quantities of same or all given or known substances (usually reactants) into moles.
- Use the coefficients in the balanced equation to calculate the number of moles of the unknown quantities (usually products)
- Using the calculated number of moles and molar masses, convert the unknown quantities to the desired units.

**DEEP Focus**

Take quantity of each reactant in terms of moles, for stoichiometric calculations as coefficients in a balanced chemical reaction represent moles.

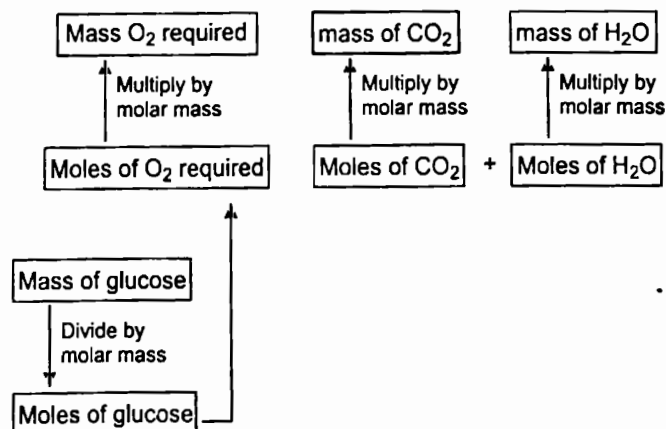
|           |                                                         |       |       |
|-----------|---------------------------------------------------------|-------|-------|
|           | $\text{A}_2 + 3\text{B}_2 \longrightarrow 2\text{AB}_2$ |       |       |
| Correct   | 1 mol                                                   | 3 mol | 2 mol |
| Incorrect | 1 g                                                     | 3 g   | 2 g   |

Mass relations in chemical reactions can be illustrated by :

**Illustration 1** Glucose,  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$  on reaction with  $\text{O}_2(\text{g})$  gives  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$



Suppose we have 18 g of glucose. Then often quantity of  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  can be determined based on stoichiometric factor. **Strategy** is that using a balanced equation, we can perform the stoichiometric calculations.



**Step I :** Balanced equation is



**Step II :** Convert amount of glucose into moles :

$$18 \text{ g glucose} = \frac{18 \text{ g}}{180 \text{ g mol}^{-1}} = 0.1 \text{ mole}$$

**Step III :** Stoichiometrically

$$\frac{\text{moles of } \text{C}_6\text{H}_{12}\text{O}_6}{\text{moles of } \text{O}_2} = \frac{1}{6}$$

$$\begin{aligned} \therefore \text{moles of } \text{O}_2 \text{ required} &= 6 \times \text{moles of } \text{C}_6\text{H}_{12}\text{O}_6 \\ &= 0.6 \text{ mole} \\ &= 0.6 \times 32 = 19.2 \text{ g} \end{aligned}$$

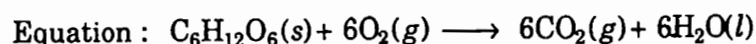
**Step IV :** Also  $\frac{\text{moles of } \text{CO}_2 \text{ formed}}{\text{moles of } \text{C}_6\text{H}_{12}\text{O}_6 \text{ reacts}} = \frac{6}{1}$

$$\therefore \text{Moles of } \text{CO}_2 \text{ formed} = 0.6 \text{ mole} = 0.6 \times 44 = 26.4 \text{ g}$$

**Step V :** Also,  $\frac{\text{moles of } \text{H}_2\text{O} \text{ formed}}{\text{moles of } \text{C}_6\text{H}_{12}\text{O}_6 \text{ reacted}} = \frac{6}{1}$

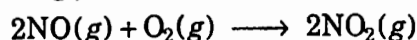
$$\therefore \text{Moles of } \text{H}_2\text{O} \text{ formed} = 0.6 \text{ mole} = 10.8 \text{ g}$$

Results can be summarised in the tabular form :



|                           |      |      |                 |                 |
|---------------------------|------|------|-----------------|-----------------|
| Initial amount (in moles) | 0.1  | 0.6  | 0               | 0               |
| change                    | -0.1 | -0.6 | +0.6            | 0.6             |
| After reaction moles      | 0    | 0    | 0.6             | 0.6             |
|                           |      |      | $0.6 \times 44$ | $0.6 \times 18$ |
|                           |      |      | 26.4 g          | 10.8 g          |

**Illustration 2** The reaction between nitric oxide (NO) and oxygen to form nitrogen dioxide ( $\text{NO}_2$ ) is a key step in photochemical smog formation:



(a) How many moles of  $\text{NO}_2$  are formed by the complete reaction of 0.25 mole of  $\text{O}_2$ ?

(b) How many gram of  $\text{NO}_2$  are formed by the complete reaction of 1.20 g of  $\text{NO}$ ?



hence,  $0.25 \text{ mol O}_2 \text{ gives } = 0.50 \text{ mol NO}_2$



1 mol  $\text{NO}$  gives = 1 mol  $\text{NO}_2$

hence,

$1.20 \text{ g NO} = \frac{1.20}{30} \text{ mol gives}$

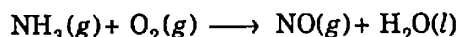
$= 1 \times \frac{1.20}{30} \text{ mol NO}_2$

$= \frac{1.20}{30} \times 46 \text{ g NO}_2$

$= 1.84 \text{ g NO}_2$

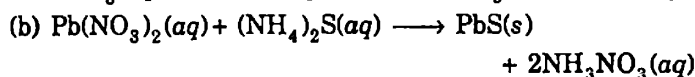
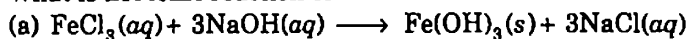
## Target Practice 1

1. Balance the following equation :

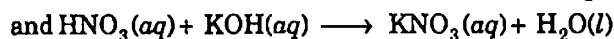
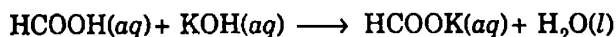


.....

2. What is net ionic reaction of

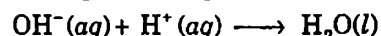


3. What is the difference in the net reactions of the following :

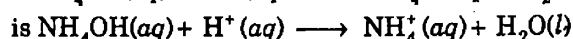
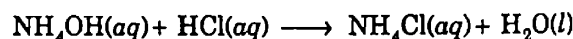


.....

4. Net reaction of



but net reaction of



Explain .....

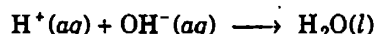
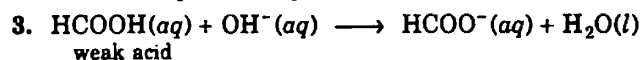
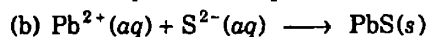
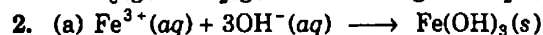
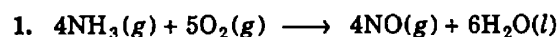
5. Which compound or compounds in each of the following groups is (are) expected to be soluble in water?

(a)  $\text{CuO}$ ,  $\text{CuCl}_2$ ,  $\text{FeCO}_3$  .....

(b)  $\text{AgI}$ ,  $\text{Ag}_3\text{PO}_4$ ,  $\text{AgNO}_3$  .....

(c)  $\text{K}_2\text{CO}_3$ ,  $\text{KI}$ ,  $\text{KMnO}_4$  .....

## Answers

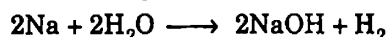


4. Since  $\text{NH}_4\text{OH}$  is a weak base

5. (a)  $\text{CuCl}_2$  (b)  $\text{AgNO}_3$  (c)  $\text{K}_2\text{CO}_3$ ,  $\text{KI}$ ,  $\text{KMnO}_4$

## Practice Exercise 1

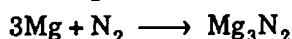
1. Consider the following reaction taking place completely



(a) How many moles of  $\text{H}_2$  will be formed from 0.46 g of  $\text{Na}$ ?

(b) How many gram of  $\text{NaOH}$  will be formed by 0.01 mole of  $\text{Na}$ ? ( $\text{Na} = 23$ ,  $\text{H} = 1$ ,  $\text{O} = 16$ )

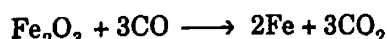
2. Consider the following reaction:



(a) Calculate amount of  $\text{Mg}$  required to prepare 10 g of  $\text{Mg}_3\text{N}_2$  in 100% reaction.

(b) How many moles of  $\text{Mg}_3\text{N}_2$  are formed from 5.6 g of  $\text{N}_2$  with excess of  $\text{Mg}$  in 100% reaction? ( $\text{Mg} = 24$ ,  $\text{N} = 14$ )

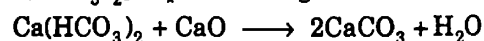
3. One of the reactions that occurs in a blast furnace, where iron ore is converted to cast iron, is



Suppose that  $1.64 \times 10^3 \text{ kg}$  of  $\text{Fe}$  are obtained from  $2.62 \times 10^3 \text{ kg}$  sample  $\text{Fe}_2\text{O}_3$ . Assuming that the reaction goes to completion, what is the per cent purity of  $\text{Fe}_2\text{O}_3$  in the original sample?

4. Select correct alternate. Only one alternate is correct.

(A) 10 L of hard water with temporary hardness of  $[\text{Ca}(\text{HCO}_3)_2]$  required 0.56 g of lime :

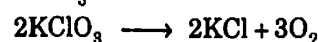


Temporary hardness in term of ppm of  $\text{CaCO}_3$  is

(a) 56 (b) 1/2

(c) 100 (d) 200

(B) 5.0 g of  $\text{KClO}_3$  gave 0.03 mole of  $\text{O}_2$ . Hence, percentage purity of  $\text{KClO}_3$  is :



(a) 49% (b) 50%

(c) 95% (d) 98%

- (C)  $\text{CaCO}_3$  is decomposed by  $\text{HCl}$  (density 1.825 g/c.c.)  
 $\text{CaCO}_3 + 2\text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$   
 Volume of  $\text{HCl}$  required to decompose 10 g of 50% pure  $\text{CaCO}_3$  is

- (a) 1.825 mL (b) 3.65 mL  
 (c) 0.9125 mL (d) 2 mL

## Answers

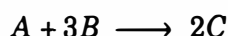
1. (a) 0.01 mol (b) 0.40 g 2. (a) 7.2 g (b) 0.2 mol  
 3. 89.42% 4. (A) (d) (B) (a) (C) (d)

## Limiting Reactants

Reactants are often carried out with an excess of one reactant over that required by stoichiometry. This is usually done to ensure that one of the reactants in the reaction is consumed completely, even though some of another reactant remains unused. The extent to which a reaction takes place depends on the amount of the reactants.

- If the reactants are present exactly in the same stoichiometric ratio as required, then no reactant is left unused.
- If one of the reactants is present in smaller quantity than as required stoichiometrically, then other reactant is left unreacted and amount of product formed is determined by the reactant which is present in smaller quantity and is called **Limiting Reactant**. The other reactant is said to be **Excess Reactant**.

**Illustration 1** In the following general example



1 mole A reacts with 3 moles B to give 2 moles C and 1 mole D. Thus, stoichiometric requirement for the reaction to go completely, is that molar ratio of A and B should be 3 : 1

$$\frac{n_A}{n_B} = 3$$

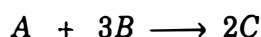
### Solution

Case I: If  $n_A = 1$

$$n_B = 2$$

i.e.,  $\frac{n_A}{n_B} = \frac{1}{2}$

then B is in smaller quantity, and amount of the products is determined by B. Thus, B is limiting reactant. We present the calculation as



Reaction says 1 mol 3 mol 2 mol  
 We take 1 mol 2 mol ?

1 mole A forms = 2 moles C

3 moles B form = 2 moles C

Thus 2 moles B form =  $\frac{4}{3} = 1.33$  moles C < 2 moles C

Also, 3 moles B react with = 1 mole A

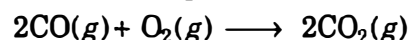
$$2 \text{ moles B react with } = \frac{2}{3} \text{ mole A} = 0.66 \text{ mole A}$$

Thus A is in excess and B reacts completely.  
 B is thus **limiting reactant**.

## Problem Solving Tips

- If you cannot decide how to solve a limiting reactant problem, do the entire calculation based on each reactant. **The smallest answer is always right**
- Moles of product formed are always determined by the starting moles of limiting reactant.

**Illustration 2** We perform the following reaction with four moles of CO and 3 moles  $\text{O}_2$ .



|               |       |       |       |
|---------------|-------|-------|-------|
| Stoichiometry | 2 mol | 1 mol | 2 mol |
| We take       | 4     | 3     | ?     |

We determine the amount of  $\text{CO}_2$  (product) based on each reactant. The reactant giving the smaller amount of  $\text{CO}_2$  will be the **limiting reactant**.

2 moles CO give = 2 moles  $\text{CO}_2$

4 moles CO give = 4 moles  $\text{CO}_2$

1 mole  $\text{O}_2$  gives = 2 moles  $\text{CO}_2$

3 moles  $\text{O}_2$  gives = 6 moles  $\text{CO}_2$

Thus, smaller quantity of the product ( $\text{CO}_2$ ) is from CO, which is thus **limiting reactant** and  $\text{O}_2$  is **excess reactant**.

**How much excess reactant ( $\text{O}_2$ ) is left**, is decided by stoichiometric ratio of the reactants or from the limiting reactant

2 moles CO consume = 1 mole  $\text{O}_2$

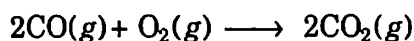
Thus, 4 moles CO consume = 2 moles  $\text{O}_2$

$$\text{Thus, } \frac{n_{\text{CO}}}{n_{\text{O}_2}} = \frac{2}{1} = \frac{4}{2}$$

Thus,  $\text{O}_2$  left unreacted =  $3 - 2 = 1$  mole

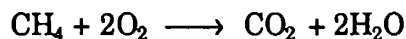
After reaction is completed, reaction mixture contains 4 moles  $\text{CO}_2$  (product) and 1 mole  $\text{O}_2$  (unreacted reactant)

We can represent the above change as



|                         |    |    |    |
|-------------------------|----|----|----|
| Stoichiometry           | 2  | 1  | 2  |
| Initial moles           | 4  | 3  | 0  |
| Change                  | -4 | -2 | +4 |
| After complete reaction | 0  | 1  | 4  |

**Illustration 3** We want to calculate the amount of  $\text{CO}_2$  formed by the reaction of 16 g  $\text{CH}_4$  with 48 g  $\text{O}_2$ .



|                       |          |          |   |   |
|-----------------------|----------|----------|---|---|
| Stoichiometry (moles) | 1        | 2        | 1 | 2 |
| We take               | 16 g     | 48 g     | ? | ? |
|                       | = 1 mole | 1.5 mole | ? | ? |

We do the calculation based on mole ratio :

$$\text{Required ratio } \frac{1 \text{ mole CH}_4}{2 \text{ moles O}_2} = \frac{0.5 \text{ mole CH}_4}{1 \text{ mole O}_2}$$

Each mole of  $\text{O}_2$  would require exactly 0.50 mole of  $\text{CH}_4$  to be completely used up

**Available ratio**

$$\frac{1 \text{ mole CH}_4}{1.5 \text{ moles O}_2} = \frac{0.67 \text{ mole CH}_4}{1 \text{ mole O}_2}$$

We have 0.67 mole of  $\text{CH}_4$  for each mole of  $\text{O}_2$ . Thus, there is  $\text{O}_2$  in small quantity and  $\text{CO}_2$  formed is decided by moles of  $\text{O}_2$

$$2 \text{ moles of } \text{O}_2 \text{ give} = 1 \text{ mole CO}_2$$

$$1.5 \text{ moles O}_2 \text{ gives} = 0.75 \text{ mole CO}_2$$

We do the calculation based on each reactant, and limiting reactant would be that give smaller amount of  $\text{CO}_2$ .

$$1 \text{ mole CH}_4 \text{ gives} = 1 \text{ mole CO}_2$$

$$2 \text{ moles O}_2 \text{ gives} = 1 \text{ mole CO}_2$$

$$1.5 \text{ moles O}_2 \text{ gives} = 0.75 \text{ mole CO}_2 \text{ (smaller)}$$

Thus,  $\text{O}_2$  is the **limiting reactant**.

**How much methane ( $\text{CH}_4$ ) is used :**

$$2 \text{ moles O}_2 \text{ consumes} = 1 \text{ mole CH}_4$$

$$1.5 \text{ moles O}_2 \text{ consumes} = 0.75 \text{ mole CH}_4$$

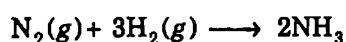
$$\text{Thus, CH}_4 \text{ left unreacted} = 1 - 0.75$$

$$= 0.25 \text{ mole CH}_4$$

$$= 4 \text{ g CH}_4$$

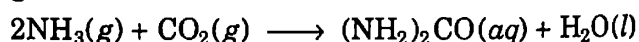
### Numerical Problem Solving 4

In the following reaction, calculate the amount formed in each case



|          |   |   |   |
|----------|---|---|---|
| Case I   | 1 | 3 | ? |
| Case II  | 2 | 3 | ? |
| Case III | 2 | 4 | ? |
| Case IV  | 1 | 1 | ? |

**Illustration 4** Urea  $(\text{NH}_2)_2\text{CO}$ , is prepared by reacting ammonia with carbon dioxide.

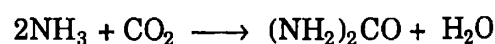


In one process, 637.2 g of  $\text{NH}_3$  are allowed to react with 1142 g of  $\text{CO}_2$  (a) Which of the two reactants is the limiting reagent? (b) Calculate the mass of  $(\text{NH}_2)_2\text{CO}$  formed (c) How much of the excess reagent (in gram) is left at the end of the reaction?

**Solution** Number of moles of

$$\text{NH}_3 \text{ taken} = \frac{637.2 \text{ g}}{17 \text{ g mol}^{-1}} = 37.482 \text{ mol}$$

$$\text{Number of moles of CO}_2 \text{ taken} = \frac{1142 \text{ g}}{44 \text{ g mol}^{-1}} = 25.955 \text{ mol}$$



(a) Limiting reagent is that one which is in smaller quantity stoichiometrically.

$$2 \text{ mol NH}_3 \text{ react with} = 1 \text{ mol CO}_2$$

$$37.482 \text{ mol NH}_3 \text{ react with} = \frac{37.482}{2} = 18.741 \text{ mol CO}_2$$

Reversely,

$$1 \text{ mol CO}_2 \text{ reacts with} = 2 \text{ mol NH}_3$$

$$25.955 \text{ mol CO}_2 \text{ reacts with} = 51.910 \text{ mol NH}_3$$

Thus,  $\text{NH}_3$  is present in **limiting quantity** and  $\text{CO}_2$  is present in excess.

(b) Quantity of the product is always determined from the limiting reactant.

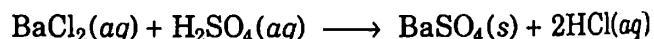
$$2 \text{ mol NH}_3 \text{ gives} = 1 \text{ mol } (\text{NH}_2)_2\text{CO}$$

$$37.482 \text{ mol NH}_3 \text{ gives} = \frac{37.482}{2} = 18.741 \text{ mol } (\text{NH}_2)_2\text{CO}$$

$$(c) \text{ CO}_2 \text{ required by } 37.482 \text{ mol of NH}_3 = 18.741 \text{ mol}$$

$$\begin{aligned} \text{Thus, CO}_2 \text{ left} &= 25.955 - 18.741 \\ &= 7.214 \text{ mol} = 7.21 \times 44 \text{ g} \\ &= 317.416 \text{ g} \end{aligned}$$

**Illustration 5** Consider following reaction :

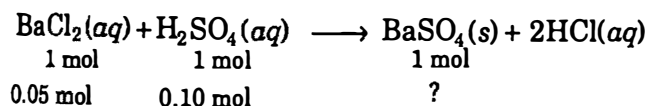


50 mL of 20.8% (w/V)  $\text{BaCl}_2(aq)$  and 100 mL of 9.8% (w/V)  $\text{H}_2\text{SO}_4(aq)$  solutions are mixed. What is the amount of  $\text{BaSO}_4(s)$  formed? Which reactant is left over after the reaction? (Ba = 137, Cl = 35.5, S = 32, H = 1, O = 16)

**Solution** Number of grams of  $\text{BaCl}_2$  present in 50 mL aqueous solution which is 20.8% (w/V) =  $\frac{20.8}{100} \times 50 = 10.4 \text{ g}$

$$\text{moles of BaCl}_2 = \frac{10.4}{208} = 0.05 \text{ mol}$$

Number of grams of  $\text{H}_2\text{SO}_4$  present in 100 mL aqueous solution which is 9.8% w/V = 9.8 g  
 moles of  $\text{H}_2\text{SO}_4 = \frac{9.8}{98} = 0.1 \text{ mol}$



1 mol  $\text{BaCl}_2$  gives = 1 mol  $\text{BaSO}_4$

0.05 mol  $\text{BaCl}_2$  gives = 0.05 mol  $\text{BaSO}_4$   
 =  $0.05 \times 233 \text{ g}$   
 = **11.65 g  $\text{BaSO}_4$**

1 mol  $\text{BaCl}_2$  reacts with = 1 mol  $\text{H}_2\text{SO}_4$

0.05 mol  $\text{BaCl}_2$  reacts with = 0.05 mol  $\text{H}_2\text{SO}_4$

But,  $\text{H}_2\text{SO}_4$  taken = 0.10 mol  $\text{H}_2\text{SO}_4$

Thus,  $\text{H}_2\text{SO}_4$  left unreacted =  $0.10 - 0.05 = 0.05 \text{ mol}$   
 =  $0.05 \times 98 \text{ g} = 4.9 \text{ g}$

Volume of  $\text{H}_2\text{SO}_4(aq)$  solution left = **50 mL** which is 9.8% (w/V).

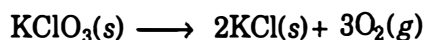
## Yields of Chemical Reactions

The maximum mass of product that can be obtained from a chemical reaction is the **theoretical yield**. Generally, loss of product occurs during the isolation and purification steps. In addition, some reactions do not go completely to products, and reactions are sometimes complicated by giving more than one set of products. For all these reasons, the **actual yield** of the product – the mass of material that is actually obtained in the laboratory or a chemical plant – is always less than the theoretical yield. In all such cases, it is desirable to report a **per cent yield**, which specifies how much of the theoretical yield was obtained, is defined as

$$\text{Per cent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

**Illustration 1**  $\text{KClO}_3(s)$  decomposes into  $\text{KCl}(s)$  and  $\text{O}_2(g)$

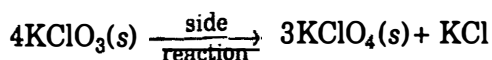
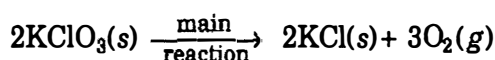
There is complete conversion of  $\text{KClO}_3$  into the products



|         |       |    |    |
|---------|-------|----|----|
| Initial | 2 mol | 0  | 0  |
| Change  | -2    | +2 | +3 |
| After   | 0     | 2  | 3  |

Thus, yield is 100%

There can be side reactions

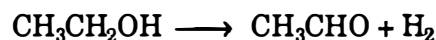


Take 2 moles of  $\text{KClO}_3(s)$  and assume product is 2 moles  $\text{O}_2(g)$  due to side reaction, then per cent yield of  $\text{O}_2(g)$  is

$$\begin{aligned} &= \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 \\ &= \frac{2}{3} \times 100 \\ &= 66.67\% \end{aligned}$$

**Illustration 2** Acetaldehyde ( $\text{CH}_3\text{CHO}$ ) can be obtained by the oxidation of ethyl alcohol ( $\text{CH}_3\text{CH}_2\text{OH}$ ).

There is no side reaction and all  $\text{CH}_3\text{CH}_2\text{OH}$  is converted to  $\text{CH}_3\text{CHO}$



Thus, yield is 100%

There can be side reaction giving acetic acid ( $\text{CH}_3\text{COOH}$ )



due to no side reaction

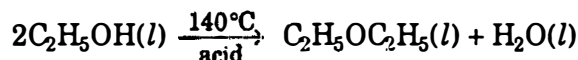
If there is also formation of 0.2 mol  $\text{CH}_3\text{COOH}$ , then yield of  $\text{CH}_3\text{CHO}$  would be 0.8 mol

$$\begin{aligned} \text{Per cent yield of } \text{CH}_3\text{CHO} &= \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 \\ &= \frac{0.8}{1} \times 100 \\ &= 80\% \end{aligned}$$

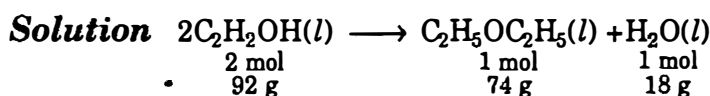
## Numerical Problem Solving 5

Acetyl chloride ( $\text{CH}_3\text{COCl}$ ) can be reduced to acetaldehyde ( $\text{CH}_3\text{CHO}$ ) in presence of  $\text{BaSO}_4/\text{Pd}$  – reaction is called Rosenmund reaction. Some ethyl alcohol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) is also obtained due to further reduction of  $\text{CH}_3\text{CHO}$  (into  $\text{CH}_3\text{CH}_2\text{OH}$ ) if experimental conditions are not efficient. In an experiment one mole of  $\text{CH}_3\text{COCl}$  gave 2.3 g  $\text{CH}_3\text{CH}_2\text{OH}$  along with  $\text{CH}_3\text{CHO}$  (main product). What is per cent yield of  $\text{CH}_3\text{CHO}$ ?

**Illustration 3** Diethyl ether ( $\text{C}_4\text{H}_{10}\text{O}$ ), the “ether” used medically as an anaesthetic, is prepared from ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) in presence of an acid



Calculate the per cent yield if 46.0 g of ethyl alcohol gives 30.0 g of ether.



Theoretical yield

92 g of  $\text{C}_2\text{H}_5\text{OH}$  gives = 74 g ether with 100% yield

$\therefore$  46 g of  $\text{C}_2\text{H}_5\text{OH}$  gives =  $\frac{74}{92} \times 46 = 37 \text{ g}$  ether with

100% yield

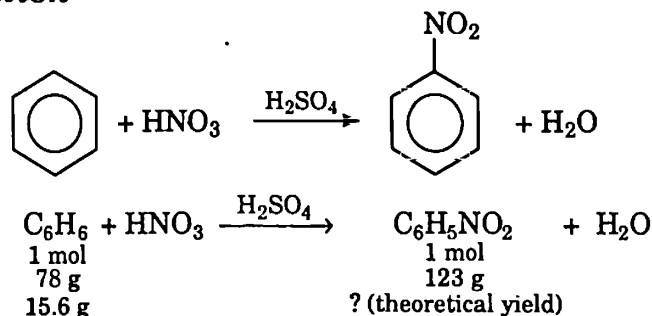
But, actual yield is = 30.0 g

$$\therefore \text{per cent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

$$= \frac{30}{37} \times 100 = 81.08\%$$

**Illustration 4** A 15.6 g sample of  $\text{C}_6\text{H}_6$  (benzene) is mixed with excess  $\text{HNO}_3$  in presence of  $\text{H}_2\text{SO}_4$ . We isolate 18.0 g of  $\text{C}_6\text{H}_5\text{NO}_2$  (nitrobenzene). What is the per cent yield of  $\text{C}_6\text{H}_5\text{NO}_2$  in this reaction?

**Solution**



Theoretical yield

$$78 \text{ g of } \text{C}_6\text{H}_6 \text{ gives} = 123 \text{ g } \text{C}_6\text{H}_5\text{NO}_2$$

$$\therefore 15.6 \text{ g of } \text{C}_6\text{H}_6 \text{ gives} = \frac{123}{78} \times 15.6 \text{ g } \text{C}_6\text{H}_5\text{NO}_2$$

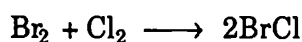
$$= 24.6 \text{ g}$$

Actual yield = 18.0 g

$$\therefore \text{per cent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

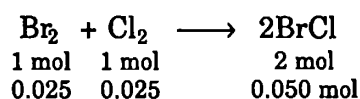
$$= \frac{18.0}{24.6} \times 100 = 73.17\%$$

**Illustration 5** The per cent yield for the following reaction carried out in carbon tetrachloride ( $\text{CCl}_4$ ) solution is 67%.



- (a) What amount of  $\text{BrCl}$  would be formed from the reaction of 0.025 mole  $\text{Br}_2$  and 0.025 mole  $\text{Cl}_2$ ?
- (b) What amount of  $\text{Br}_2$  is left unchanged?

**Solution**



(a) Theoretical yield of  $\text{BrCl} = 0.050 \text{ mol}$

$$\text{actual yield of } \text{BrCl} = 0.050 \times \frac{67}{100}$$

$$= 0.0335 \text{ mol}$$

$$(b) \text{Br}_2 \text{ reacted} = 0.025 \times \frac{67}{100} = 0.01675 \text{ mol}$$

$$\text{Br}_2 \text{ left unreacted} = 0.025 - 0.01675 = 0.00825 \text{ mol}$$

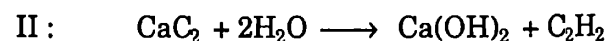
## Sequential Reactions

Often more than one reaction is required to change starting materials into the desired product. This is true for many reactions that we carry out in the laboratory and for

many industrial process. These are called sequential reactions. The amount of desired product from each reaction is taken as the starting material for the next reaction. We consider following illustrations.



$\text{KClO}_3$  decomposes in step I to give  $\text{O}_2$ , which in turn, is used by  $\text{Al}$  to form  $\text{Al}_2\text{O}_3$  in step II. First we determine  $\text{O}_2$  formed in step I and then  $\text{Al}$  used by this  $\text{O}_2$  in step II. Both reactions can be added to determine amount of  $\text{KClO}_3$  that can give required amount of  $\text{O}_2$  needed for  $\text{Al}$ .



$\text{CaC}_2$  (calcium carbide) is prepared in step I. It is used to prepare acetylene ( $\text{C}_2\text{H}_2$ ) in step II. Suppose we want to determine amount of  $\text{CaO}$  that can give enough  $\text{CaC}_2$  to be converted into required amount of  $\text{C}_2\text{H}_2$ . Amount of  $\text{CaO}$  is determined in step I and then amount of  $\text{C}_2\text{H}_2$  in step II. We can relate  $\text{CaO}$  and  $\text{C}_2\text{H}_2$  stoichiometrically by writing net reaction which is

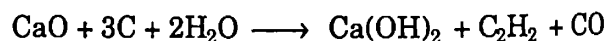
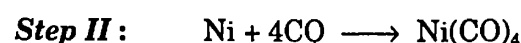
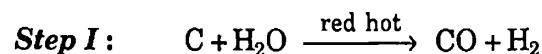
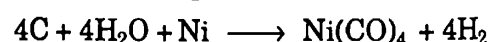


**Illustration 3** Purification of  $\text{Ni}$  in Mond's process is based on the conversion of  $\text{Ni}$  (impure) into pure  $\text{Ni(CO)}_4$ , using  $\text{CO}$  (step II) which in turn is obtained in step I



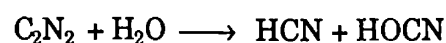
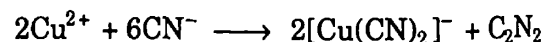
If we combine both steps then



## Numerical Problem Solving 6

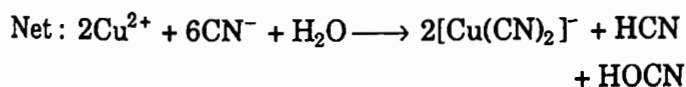
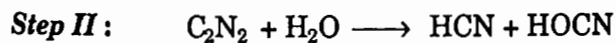
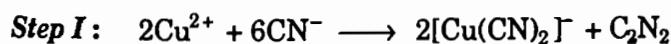
Take illustration (3) given above. What mass of  $\text{Ni(CO)}_4$  could be obtained from the  $\text{CO}$  produced by the reaction of 72 g carbon? Assume 100% reaction and 100% recovering in both cases. ( $\text{Ni} = 58.7$ )

**Illustration 4** Consider the formation of cyanogen,  $\text{C}_2\text{N}_2$ , and its subsequent decomposition in water given by the equations :



How much hydrocyanic acid, HCN, can be produced from 20.0 g of KCN, assuming 100% yield?  
(H = 1, C = 12, N = 14, K = 39)

### Solution



Thus, 6 mol KCN gives = 1 mol HCN

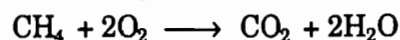
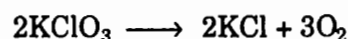
$$\therefore \frac{20}{65} \text{ mol KCN gives} = \frac{20}{65 \times 6} \text{ mol HCN}$$

$$= 0.05128 \text{ mol HCN}$$

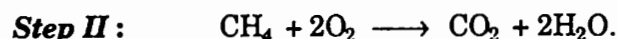
$$= 0.05128 \times 27 \text{ g HCN}$$

$$= 1.38462 \text{ g HCN}$$

**Illustration 5** What mass of potassium chlorate ( $\text{KClO}_3$ ) would be required to supply the proper amount of oxygen needed to burn 33.2 g of methane ( $\text{CH}_4$ )?

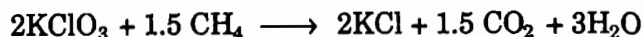


$$(\text{K} = 39, \text{O} = 16, \text{C} = 12, \text{H} = 1, \text{Cl} = 35.5)$$



$\text{KClO}_3$  gives  $\text{O}_2$ , and  $\text{O}_2$  in turn is used to combust  $\text{CH}_4$ . Thus,  $\text{O}_2$  is the intermediate reactant. To cancel out  $\text{O}_2$  multiply step II reaction by 1.5, thus,

**Net reaction is**



$$1.5 \text{ mol of CH}_4 \text{ is combusted by O}_2 \text{ supplied by} \\ = 2 \text{ mol KClO}_3$$

$$\text{hence, } \frac{33.2}{16} \text{ mol of CH}_4 \text{ is combusted by O}_2 \text{ supplied by}$$

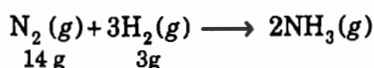
$$= \frac{2}{1.5} \times \frac{33.2}{16} \text{ mol KClO}_3$$

$$= 2.767 \text{ mol KClO}_3$$

$$= 338.92 \text{ g}$$

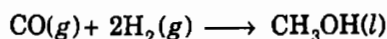
## Target Practice 2

1. Which is the limiting reactant in the following?



2. What is the amount of the product,  $\text{NH}_3$  in the question (1) react?

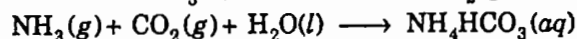
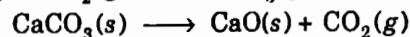
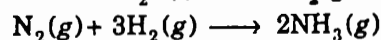
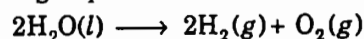
3. Carbon monoxide ( $\text{CO}$ ) and hydrogen ( $\text{H}_2$ ) react to form methanol ( $\text{CH}_3\text{OH}$ )



How much  $\text{CH}_3\text{OH}(\text{l})$  obtained from 0.01 mole  $\text{CO}(\text{g})$  and 0.08 g  $\text{H}_2(\text{g})$ ?

4. 50 g of calcium carbonate sample,  $\text{CaCO}_3$ , (lime stone) gave 1.12 L carbon dioxide gas measured at STP. (1 mole of every ideal gas at STP has 22.4 L volume)  
What is per cent purity of  $\text{CaCO}_3$ ?

5. Take following sequential reactions :

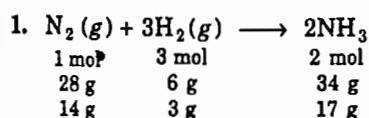


We want to produce 0.10 mol  $\text{NH}_4\text{HCO}_3$ .

$\text{H}_2\text{O}(\text{l})$  required is .....

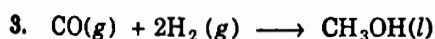
$\text{N}_2(\text{g})$  required is .....

## Answers



Both  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$  are in exact quantity.

2. 17 g (as in question (1))



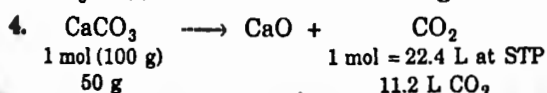
$$\begin{array}{ccc} 1 \text{ mol} & 2 \text{ mol} & 1 \text{ mol} \\ 0.01 \text{ mol} & 0.02 \text{ mol} & 0.01 \text{ mol} \\ 0.02 \text{ mol} & 0.04 \text{ mol} & 0.02 \text{ mol} \end{array}$$

$$\text{CO}(\text{g}) = 0.01 \text{ mol}$$

$$\text{H}_2(\text{g}) = 0.08 \text{ g} = 0.04 \text{ mol}$$

Thus,  $\text{CO}(\text{g})$  is limiting reagent

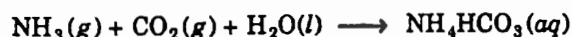
$$\text{CH}_3\text{OH}(\text{l}) \text{ formed} = 0.01 \text{ mol} = 0.32 \text{ g}$$



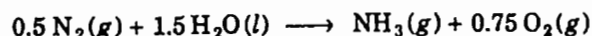
But actual yield = 1.12 L  $\text{CO}_2$  from 5.0 g pure  $\text{CaCO}_3$

$$\therefore \text{Per cent purity} = \frac{5}{50} \times 100 = 10\% \text{ pure}$$

5. (a)  $2\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \times 0.75$   
(b)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g}) \times 0.50$   
(c)  $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$



0.75(a) + 0.50(b) gives



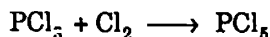
Thus,  $\text{N}_2(\text{g})$  required = 0.05 mol for 0.1 mol  $\text{NH}_4\text{HCO}_3$

$\text{H}_2\text{O}(\text{l})$  required = 0.15 mol in (a) and (b) + 0.10 mol in final reaction = 0.25 mol



## Practice Exercise 2

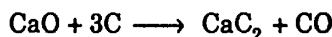
1. The per cent yield for the reaction



is 83.2%. What mass of  $\text{PCl}_5$  would be expected from the reaction of 56.7 g of  $\text{PCl}_3$  with excess  $\text{Cl}_2$ ?

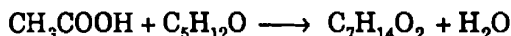
(P = 31, Cl = 35.5)

2. Calcium carbide is made in an electric-furnace by the reaction:

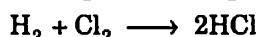
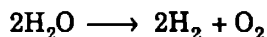


The crude product is usually 85%  $\text{CaC}_2$  and 15% unreacted  $\text{CaO}$ . (a) How much  $\text{CaO}$  should we start with to produce 450 kg of crude product? (b) How much  $\text{CaC}_2$  would this crude product contain? (Ca = 40, C = 12, O = 16)

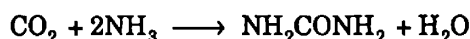
3. If 1.87 g of acetic acid (
- $\text{CH}_3\text{COOH}$
- ) reacts with 2.31 g of isopentyl alcohol (
- $\text{C}_5\text{H}_{12}\text{O}$
- ) to give 2.96 g isopentyl acetate (
- $\text{C}_7\text{H}_{14}\text{O}_2$
- ), what is the per cent yield of the reaction?



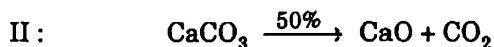
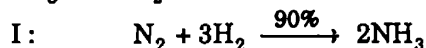
4. Hydrogen, obtained by the electrical decomposition of water, was combined with chlorine to produce 62.5 g of hydrogen chloride. Calculate the mass of water decomposed.



5. Urea,
- $\text{NH}_2\text{CONH}_2$
- , is formed when
- $\text{CO}_2$
- reacts with
- $\text{NH}_3$



$\text{NH}_3$  and  $\text{CO}_2$  are obtained in the following steps



Calculate amount of  $\text{N}_2$  and  $\text{CaCO}_3$  to produce 60 kg of urea.

6. The reaction between aluminium and iron (III) oxide can generate temperature approaching 3000°C and is used in welding metals:

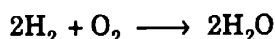


In one process 124 g Al are reacted with 601 g of  $\text{Fe}_2\text{O}_3$ .

(a) Calculate the number of moles of  $\text{Al}_2\text{O}_3$  formed.

(b) How much of the excess reagent is left at the end of the reaction? (Al = 27, Fe = 56, O = 16)

- 7.
- $\text{H}_2\text{O}$
- can be obtained from by the reaction



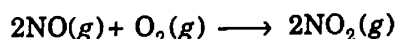
If we take 1 mol  $\text{O}_2$  and 1 g  $\text{H}_2$ ,

(a) Which is the limiting reactant?

(b) How much of the excess reactant is left unreacted?

(c) How much of  $\text{H}_2\text{O}$  is formed?

8. Nitric oxide (NO) reacts instantly with oxygen gas to form nitrogen dioxide (
- $\text{NO}_2$
- ), a dark-brown gas



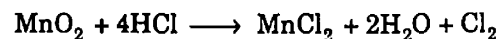
In one experiment 1.0 mol of NO is mixed with 1.0 mol of  $\text{O}_2$

(a) Calculate which of the two reactants is the limiting reagent.

(b) Calculate also the number of mol of  $\text{NO}_2$  produced.

9. Select correct alternate. Only one alternate is correct.

(A) In the following reaction:



2 moles  $\text{MnO}_2$  reacts with 4 moles of HCl to form 11.2 L  $\text{Cl}_2$  at STP. Thus, per cent yield of  $\text{Cl}_2$  is

- (a) 25% (b) 50%  
(c) 100% (d) 75%

(B) 2 moles of 50% pure  $\text{Ca}(\text{HCO}_3)_2$  on heating forms 1 mole of  $\text{CO}_2$ . Thus, per cent yield of  $\text{CO}_2$  is

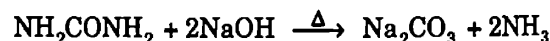


- (a) 50% (b) 75%  
(c) 80% (d) 100%

(C) Mixture of 1 mole of  $\text{Na}_2\text{CO}_3$  and 2 moles of  $\text{NaHCO}_3$  forms 1 mole of  $\text{CO}_2$  on heating. Thus, per cent yield of  $\text{CO}_2$  is

- (a) 25% (b) 50%  
(c) 75% (d) 100%

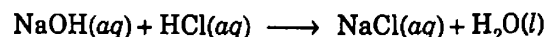
(D) Per cent yield of  $\text{NH}_3$  in the following reaction is 80%



6 g  $\text{NH}_2\text{CONH}_2$  reacts with 8 g NaOH to form  $\text{NH}_3$

- (a) 3.4 g (b) 2.72 g  
(c) 4.25 g (d) 11.2 g

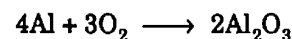
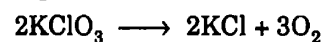
(E) 100 mL solution of NaOH (containing 4 g NaOH per litre) and 50 mL of HCl (containing 7.3 g HCl per litre) react as:



0.5 g of NaCl is formed. Thus, unreacted NaOH is

- (a) 0.058 g (b) 3.66 g  
(c) 10.8 g (d) 0.63 g

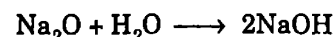
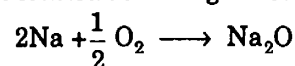
(F) Al and  $\text{KClO}_3$  react together to form  $\text{Al}_2\text{O}_3$  according to



4 moles of  $\text{KClO}_3$  (50% pure) on reaction with excess of Al forms  $\text{Al}_2\text{O}_3$

- (a) 2 mol (b) 4 mol  
(c) 6 mol (d) 8 mol

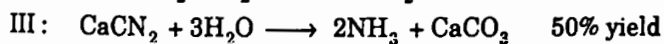
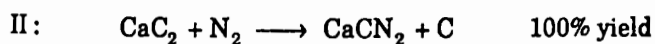
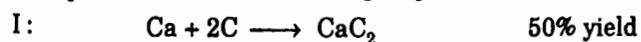
(G) NaOH is formed according to reaction



To make 4 g NaOH, Na required is

- (a) 4.6 g (b) 4.0 g  
(c) 2.3 g (d) 0.23 g

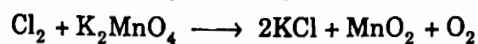
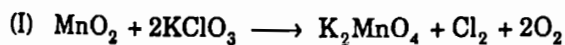
(H)  $\text{NH}_3$  is formed in the following steps



To obtain 2 moles  $\text{NH}_3$ , calcium required is

(a) 1 mol (b) 2 mol

(c) 3 mol (d) 4 mol



Each reaction takes place to the extent of 50%. 11.2 L of  $\text{O}_2$  at STP is obtained from  $\text{KClO}_3$  using

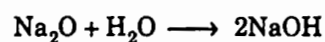
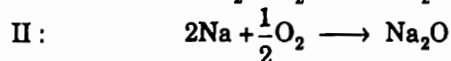
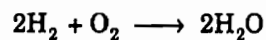
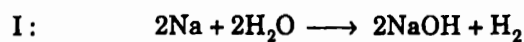
(a) 0.67 mol

(b) 1.12 mol

(c) 1.33 mol

(d) 2.66 mol

(J)  $\text{NaOH}$  can be prepared by two methods each with two steps having 100% extent.



Which gives better yield?

(a) I

(b) II

(c) Both equal

(d) None is suitable

## Answers

1. 71.53 g 2. (a) 393.75 kg (b) 382.50 kg

3. 86.74% 4. 15.411 g

5. 31.111 kg  $\text{N}_2$ , 200 kg  $\text{CaCO}_3$

6. (a) 2.296 mol (b) 1.46 mol

7. (a)  $\text{H}_2$  (b)  $\text{O}_2$  left = 24 g = 0.75 mol (c) 9 g  $\text{H}_2\text{O}$

8. (a)  $\text{NO}$  is the limiting reactant (b) 1 mol  $\text{NO}_2$

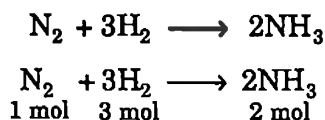
9. (A) (b) (B) (a) (C) (d) (D) (b) (E) (a)

(F) (a) (G) (c) (H) (d) (I) (a) (J) (c)

# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** Assume that you have 1.39 moles of  $N_2$  and 3.44 moles of  $H_2$ . (a) How many grams of ammonia ( $NH_3$ ) can you make? (b) How many grams of which reactant will be left over? (c) How many grams of the limiting reactant will be required to react with the reactant present in larger amount?



**Plan**  $N_2$  and  $H_2$  react in 1:3 mol ratio. Reactant present in smaller quantity (in terms of mol) stoichiometrically is the limiting reactant and the other present in larger quantity is left over. Thus, amount of  $NH_3$  reactant left over and the reactant required for complete reaction can be calculated.

**Solution** Number of moles of  $N_2 = 1.39 \text{ mol}$

Number of moles of  $H_2$  taken = 3.44 mol

Number of moles of  $H_2$  required by 1.39 moles of  $N_2 = 1.39 \times 3 = 4.17 \text{ mol}$

Thus,  $H_2$  is present in **smaller quantity** and is thus the **limiting reactant**.

(a) 3 mol of  $H_2$  gives = 2 mol  $NH_3$   
 $3.44 \text{ mol gives} = \frac{2}{3} \times 3.44$   
 = **2.293 mol  $NH_3$**

(b) 3 mol of  $H_2$  react with = 1 mol  $N_2$   
 $3.44 \text{ mol } H_2 \text{ react with} = \frac{1}{3} \times 3.44 = 1.147 \text{ mol } N_2$

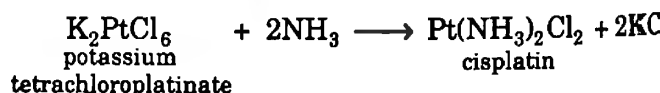
Thus, number of  $N_2$  left over =  $1.390 - 1.147$   
 = **0.243 mol**

(c) Number of moles of

$H_2$  required by 1.39 mol  $N_2 = 4.17 \text{ mol}$

Number of moles of  $H_2$  actually present = 3.44 mol  
 Additional  $H_2$  required =  $4.17 - 3.44$   
 = **0.73 mol**

**Problem 2.** Cisplatin, an anticancer agent used for the treatment of solid tumours, is prepared by the reaction of ammonia with potassium tetra chloroplatinate:



Assume that 10.0 g of  $K_2PtCl_4$  and 10.0 g of  $NH_3$  are allowed to react.

- (a) Which reactant is limiting and which is in excess?  
 (b) How many grams of the excess reactant are consumed, and how many gram remain?  
 (c) How many grams of cisplatin are formed?  
 (Pt = 195, K = 39, Cl = 35.5, N = 14, H = 1)

**Plan** Given amounts are converted into moles. Limiting reactant is that which is present stoichiometrically in smaller amount. Quantity of the product is always determined from the limiting reactant.

**Solution** Number of moles of

$$K_2PtCl_4 = \frac{10 \text{ g}}{415 \text{ g mol}^{-1}} = 0.0241 \text{ mol}$$

$$\text{Number of moles of } NH_3 = \frac{10}{17} = 0.5882 \text{ mol}$$

Moles of  $NH_3$  required by 0.0241 moles of  $K_2PtCl_4$   
 = 0.0482 mol

but,  $NH_3$  taken = 0.5882 mol  $\gg$  0.0482 mol

(a) Thus,  $K_2PtCl_4$  is the **limiting reactant** and  $NH_3$  is in excess.

(b)  $NH_3$  consumed = 0.0482 mol =  $0.0482 \times 17 \text{ g}$   
 = **0.8194 g**

$NH_3$  left =  $10 - 0.8194 = \mathbf{9.1806 \text{ g}}$

(c) 1 mole of  $K_2PtCl_4$  gives = 1 mol of  $Pt(NH_3)_2Cl_2$   
 cisplatin

$\therefore$  0.0241 mole  $K_2PtCl_4$  gives = 0.0241 mol  $Pt(NH_3)_2Cl_2$   
 =  $0.0241 \times 300 \text{ g}$   
 = **7.23 g**

**Problem 3.** At high temperatures carbon reacts with water to produce a mixture of carbon monoxide, CO and hydrogen,  $H_2$ .



CO is separated from  $H_2$ , and then used to separate nickel from cobalt by forming a volatile compound, nickel tetracarbonyl,  $Ni(CO)_4$ .



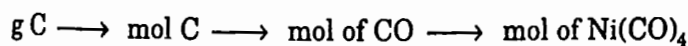
What mass of  $Ni(CO)_4$  could be obtained from the CO produced by the reaction of 75.0 g of carbon? Assume 100% reaction and 100% recovery in both steps. ( $Ni = 59$ )

**Plan** We determine the number of moles of CO formed in the first reaction.

From the number of moles of CO produced in the first reaction, we calculate the number of grams of  $Ni(CO)_4$  that would be formed in the second reaction. Or, if we combine both the reactions

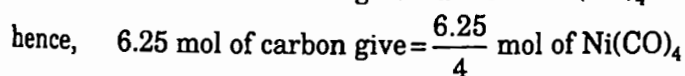
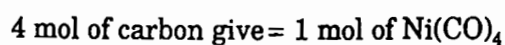


we find that 4 moles carbon gives = 1 mole of  $Ni(CO)_4$ .



**Solution** Number of mol of carbon

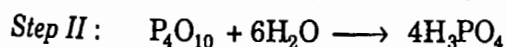
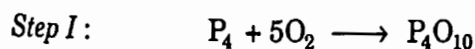
$$= \frac{75\ \text{g}}{12\ \text{g mol}^{-1}} = 6.25\ \text{mol}$$



$$= \frac{6.25}{4} \times 171\ \text{g}$$

$$= 267.2\ \text{g}$$

**Problem 4.** Phosphoric acid, ( $H_3PO_4$ ) is widely used to make fertilizers, and can be prepared in a two-step process.



We allow 272 g of phosphorus to react with excess oxygen, which forms tetraphosphorus decoxide ( $P_4O_{10}$ ) in 89.5% yield. In the step II reaction, 96.8% yield of  $H_3PO_4$  is obtained. What mass of  $H_3PO_4$  is obtained? ( $P = 31, H = 1, O = 16$ )

**Plan** We convert amount of  $P_4$  given into number of moles. Also 1 mole  $P_4 \equiv 1$  mole  $P_4O_{10}$  thus, number of moles (with 89.5% yield) of  $P_4O_{10}$  are known.

Also 1 mole of  $P_4O_{10}$  gives 4 moles of  $H_3PO_4$  in step II. Thus, amount of  $H_3PO_4$  is also known (with 96.8% yield).

**Solution** In Step I: Number of mol of  $P_4$

$$= \frac{272\ \text{g}}{4 \times 31\ \text{g mol}^{-1}} = 2.1935$$

$$\text{Theoretical } P_4O_{10}\ \text{formed} = 2.1935\ \text{mol}$$

$$\text{Actual } P_4O_{10}\ \text{formed} = 2.1935 \times \frac{89.5}{100}$$

$$= 1.9632\ \text{mol}$$

In Step II: Theoretical  $H_3PO_4$  formed

$$= 4 \times \text{moles of } P_4$$

$$= 4 \times 1.9632\ \text{mol } H_3PO_4$$

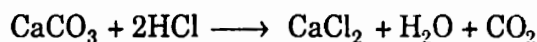
$$\text{Actual } H_3PO_4\ \text{formed} = 4 \times 1.9632 \times \frac{96.8}{100}$$

$$= 7.6016\ \text{mol}$$

$$= 7.6016\ \text{mol} \times 98\ \text{g mol}^{-1}$$

$$= 744.96\ \text{g}$$

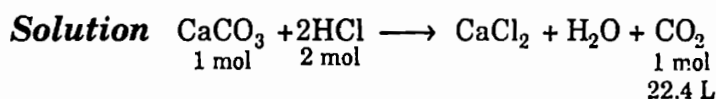
**Problem 5.** Lime stone ( $CaCO_3$ ) reacts with hydrochloric acid according to the equation:



If 1.00 mole of  $CO_2$  has a volume of 22.4 L under the reaction conditions, how many litres of gas can be formed by the reaction of 2.35 g of  $CaCO_3$  with 2.35 g of  $HCl$ ? Which reactant is limiting?

**Plan** Quantity of the product is always determined from the reactant present stoichiometrically in smaller amount (expressed in terms of moles)

Reactant present in smaller amount is the limiting reactant. ( $Ca = 40, C = 12, O = 16, Cl = 35.5, H = 1$ )



$$CaCO_3 = \frac{2.35}{100} = 0.0235\ \text{mol}$$

$$HCl = \frac{2.35}{36.5} = 0.0644\ \text{mol}$$

$$1\ \text{mol } CaCO_3\ \text{requires} = 2\ \text{mol } HCl$$

$$\therefore 0.0235\ \text{mol } CaCO_3\ \text{requires} = 0.0470\ \text{mol } HCl$$

$$HCl\ \text{taken} = 0.0644\ \text{mol}$$

Thus,  $HCl$  is present in excess and amount of the product is determined from  $CaCO_3$ , which is the limiting reactant.

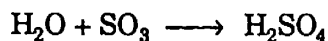
$$1\ \text{mol } CaCO_3\ \text{gives} = 1\ \text{mol } CO_2 = 22.4\ \text{L } CO_2$$

$$0.0235\ \text{mol } CaCO_3\ \text{gives} = 0.5264\ \text{L } CO_2$$

**Problem 6.** What is the per cent free  $SO_3$  in an oleum ( $H_2S_2O_7$ ) that is labelled "109%  $H_2SO_4$ "?

**Plan** Such a label refers to the total mass of pure  $H_2SO_4$ , 109 g, that would be present after dilution of 100 g of the oleum, when all free  $SO_3$  would combine with water to form  $H_2SO_4$ .

**Solution** 9 g of  $\text{H}_2\text{O}$  is mixed with 100 g oleum



Since, 18 g  $\text{H}_2\text{O}$  combines with 80 g  $\text{SO}_3$

9 g  $\text{H}_2\text{O}$  combines with 40 g  $\text{SO}_3$

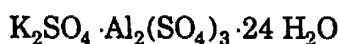
thus, 100 g of oleum has 40 g  $\text{SO}_3$

40% free  $\text{SO}_3$  in oleum

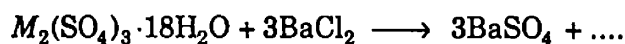
**Problem 7.** A 0.7160 g of a hydrated metallic sulphate of formula  $M_x(\text{SO}_4)_y \cdot 18\text{H}_2\text{O}$  precipitated 0.7002 g of  $\text{BaSO}_4$ . When mixed with  $\text{K}_2\text{SO}_4$  and crystallised, the metallic sulphate yielded an alum isomorphous with potash alum. Find the atomic weight of the metal.

**Plan**  $M_x(\text{SO}_4)_y \cdot 18\text{H}_2\text{O}$  is isomorphous with alum with formula  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  thus,  $x = 2$ , and  $y = 3$ . From the stoichiometric amount of  $\text{BaSO}_4$ , and given amount of  $\text{BaSO}_4$ , atomic weight of  $M$  is determined.

**Solution** Crystallised substance formed with  $\text{K}_2\text{SO}_4$  is isomorphous with alum,



Thus,  $M$  is trivalent,  $M^{3+}$  and hydrated metallic sulphate is  $M_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$



1 mol of hydrated salt gives = 3 mol of  $\text{BaSO}_4$

or  $(2M + 612)$  g of hydrated salt gives =  $3 \times 233$  g  $\text{BaSO}_4$

0.7160 g of hydrated salt gives

$$= \frac{3 \times 233}{(2M + 612)} \times 0.7160 \text{ g BaSO}_4$$

$$\therefore \frac{3 \times 233 \times 0.7160}{(2M + 612)} = 0.7002 \text{ g (given)}$$

$$(2M + 612) = 714.77$$

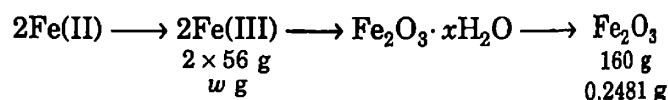
$$2M = 102.77$$

$$M = 51.38$$

**Problem 8.** A 0.4852-g sample of iron-ore is dissolved in acid, and iron is oxidised to the +3 state and the precipitated as the hydrous oxide,  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ . The precipitate is filtered, washed and ignited to  $\text{Fe}_2\text{O}_3$ , which is found to weigh 0.2481 g. Calculate the percentage of iron (Fe) in the sample. (Fe = 56, O = 16)

**Plan** Only Fe(II) in the pure state after oxidation to Fe(III) is precipitated as  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  which gives  $\text{Fe}_2\text{O}_3$ . From the weight of  $\text{Fe}_2\text{O}_3$ , percentage of iron in iron-ore can be determined.

**Solution** Let iron in iron-ore be =  $w$  g



$$\text{Thus, } \frac{w}{2 \times 56} = \frac{0.2481}{160}$$

$$\therefore w = \frac{0.2481}{160} \times 2 \times 56 \text{ g pure Fe(II)}$$

$$= 0.1737 \text{ g in 0.4852 g sample}$$

$$\text{Thus, percentage of Fe(II)} = \frac{0.1737 \times 100}{0.4852}$$

$$= 35.80$$

# Master Exercises

## Exercise 1 (Stage 1 : Learning)

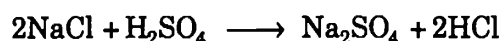
### Short Answer Type Questions

1. Classify following as soluble or insoluble salts in water.  $\text{FeS}$ ,  $\text{PbS}$ ,  $\text{CaSO}_4$ ,  $\text{NaOH}$ ,  $\text{CaO}$ ,  $\text{CaCO}_3$ ,  $\text{CaC}_2\text{O}_4$
2. What is driving force in a precipitation reaction?
3. What is driving force in a neutralisation reaction?
4. One mole of  $\text{HCl(aq)}$  is neutralised by one mole of  $\text{NaOH(aq)}$ . If we take  $\text{Ca(OH)}_2\text{(aq)}$ , then how many moles of  $\text{Ca(OH)}_2$  are required?
5. Calculate moles of  $\text{H}_2\text{SO}_4$  required to complete reaction of
  - (i) 1 mole  $\text{Ca(OH)}_2$
  - (ii) 1 mole  $\text{KOH}$
6. Consider the reaction
$$2\text{NO} + \text{Br}_2 \longrightarrow 2\text{NOBr}$$
For every 5.00 moles of bromine that reacts, how many moles of
  - (a) NO react and
  - (b) NOBr are produced?
7. What mass of  $\text{ClO}_2$  is required to produce 8.36 kg of  $\text{HClO}_3$  by the following reaction?
$$2\text{ClO}_2 + \text{H}_2\text{O} \longrightarrow \text{HClO}_3 + \text{HClO}_2$$
8. We allow 32.0 g of methane,  $\text{CH}_4$ , to react as completely as possible with excess of  $\text{O}_2$ , to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .
  - (a) Write the balanced equation
  - (b) What mass of oxygen will react?
9. What mass of pentane,  $\text{C}_5\text{H}_{12}$ , produce  $3.01 \times 10^{22}$   $\text{CO}_2$  molecules when burnt in excess oxygen  $\text{O}_2$ .
10. Lime,  $\text{CaO}$ , dissolved in muriatic acid,  $\text{HCl}$ , to form calcium chloride,  $\text{CaCl}_2$ , and water,  $\text{H}_2\text{O}$ 
  - (a) How many moles of  $\text{HCl}$  would be required to dissolve 8.8 moles of  $\text{CaO}$
  - (b) How many moles of  $\text{H}_2\text{O}$  would be formed?

11. What mass of potassium can be produced by the reaction of 150.0 g of Na with 150.0 g of  $\text{KCl}$ ?



12. How much 74.1% pure  $\text{Na}_2\text{SO}_4$  could be produced from 245 g of 93.9% pure  $\text{NaCl}$ ?



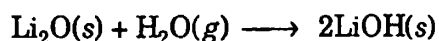
### Analytical Questions

#### Stoichiometry

1. Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), used as a solvent, is prepared by reaction of methane ( $\text{CH}_4$ ) with chlorine ( $\text{Cl}_2$ ). How many grams of  $\text{CH}_2\text{Cl}_2$  result from reaction of 1.85 kg of methane if the yield is 43.1%?
2. 4 g of a mixture of dry sodium carbonate and sodium bicarbonate containing 75% of the latter was heated until there was no loss in the weight. Calculate volume of  $\text{CO}_2$  evolved at STP.
3. Find the volume of hydrogen which would be evolved at STP by reacting zinc with 50 mL of 40% pure dil.  $\text{H}_2\text{SO}_4$  (density = 1.3 g / mL).

#### Limiting Reactants

4. Lithium oxide, ( $\text{Li}_2\text{O}$ ) is used aboard the space shuttle to remove water from the air supply according to the equation



If there are 80.0 kg of water to be removed and 65 kg of  $\text{Li}_2\text{O}$  available, which reactant is limiting? How many kilograms of the excess reactant remain? ( $\text{Li} = 7, \text{O} = 16, \text{H} = 1$ )

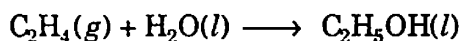
5. Consider the reaction



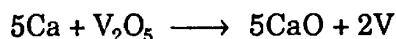
If 0.86 mole of  $\text{MnO}_2$  and 48.2 g of  $\text{HCl}$  react, which reagent will be used up first? How many gram of  $\text{Cl}_2$  will be produced? ( $\text{Mn} = 55$ ,  $\text{O} = 16$ ,  $\text{Cl} = 35.5$ )

### Yields of Chemical Reactions

6. Ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) is prepared industrially by the reaction of ethylene ( $\text{C}_2\text{H}_4$ ) with water. What is the per cent yield of the reaction if 9.6 g of ethylene gives 4.7 g of ethyl alcohol?



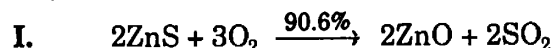
7. Industrially, vanadium metal can be obtained by reacting vanadium (V) oxide with calcium at high temperatures



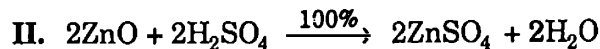
In one process,  $1.54 \times 10^3$  g of  $\text{V}_2\text{O}_5$  react with  $1.96 \times 10^3$  g of  $\text{Ca}$ , (a) Calculate the theoretical yield of  $\text{V}$ . (b) Calculate the per cent yield if 803 g of  $\text{V}$  are obtained. ( $\text{Ca} = 40$ ,  $\text{V} = 51$ ,  $\text{O} = 16$ )

### Sequential Reactions

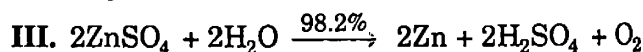
8. The chief ore of zinc is the sulphide,  $\text{ZnS}$ . The ore is concentrated by floatation process and then heated in air, which converts the  $\text{ZnS}$  to  $\text{ZnO}$ .



The  $\text{ZnO}$  is then treated with dilute  $\text{H}_2\text{SO}_4$



to produce  $\text{ZnSO}_4(aq)$  which produces  $\text{Zn}$  metal on electrolysis.



What mass of  $\text{Zn}$  will be obtained from an ore containing 225 kg of  $\text{ZnS}$ ? Efficiencies of the processes have been indicated above the arrow mark. ( $\text{Zn} = 65$ ,  $\text{S} = 32$ ,  $\text{O} = 16$ ,  $\text{H} = 1$ )

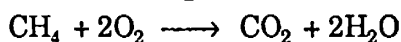
9. How many grams of calcium carbonate are required to produce enough carbon dioxide which can convert 0.5 mole of sodium carbonate into sodium bicarbonate?

## Exercise 2

### (Stage 2 : High Skill Problem Solving)

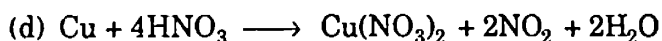
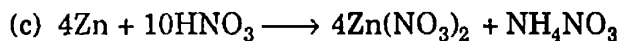
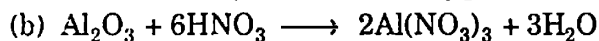
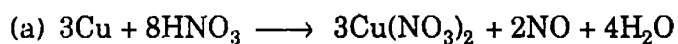
#### Only One Option Correct

1. What mass of  $\text{CO}_2$  could be formed by the reaction of 16 g  $\text{CH}_4$  with 48 g of  $\text{O}_2$ ?



- (a) 44 g (b) 33 g  
(c) 16 g (d) 24 g

2. For the formation of 5.00 mol of water, which reaction uses the most nitric acid?



3. One mole of  $\text{SO}_2\text{Cl}_2$  is dissolved in water and  $\text{Ca}(\text{OH})_2$  is added to neutralise acidic solution. Moles of  $\text{Ca}(\text{OH})_2$  required are

- (a) 2 (b) 3  
(c) 4 (d) 5

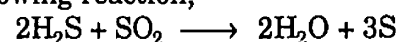
4. 0.5 mole of  $\text{BaCl}_2$  is mixed with 0.2 mole of  $(\text{NH}_4)_3\text{PO}_4$ . Maximum number of moles of barium phosphate formed in this reaction is

- (a) 0.1 (b) 0.2  
(c) 0.3 (d) 0.5

5. Reactant present in excess (with extra number of moles of that reactant) in question (4) above is

- (a)  $\text{BaCl}_2$ , 0.3 mol (b)  $(\text{NH}_4)_3\text{PO}_4$ , 0.2 mol  
(c)  $(\text{NH}_4)_3\text{PO}_4$ , 0.1 mol (d)  $\text{BaCl}_2$ , 0.2 mol

6. In the following reaction,



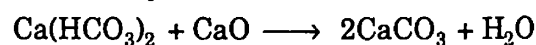
1 mol each of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  will give sulphur

- (a) 1 mol (b) 3 mol  
(c) 1.5 mol (d) 2 mol

7. One mole  $\text{BaF}_2$  is treated with two moles of  $\text{H}_2\text{SO}_4$ . To make the resulting mixture neutral,  $\text{NaOH}$  is added.  $\text{NaOH}$  required in this process is

- (a) 4 mol  $\text{NaOH}$  (b) 2 mol  $\text{NaOH}$   
(c) 3 mol  $\text{NaOH}$  (d) 1 mol  $\text{NaOH}$

8. Temporary hardness is due to  $\text{HCO}_3^-$  of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . It is removed by addition of  $\text{CaO}$ .

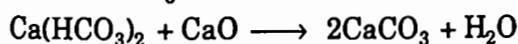


Mass of  $\text{CaO}$  required to precipitate 2 g  $\text{CaCO}_3$  is

- (a) 2.00 g (b) 0.56 g  
(c) 0.28 g (d) 1.12 g

9. Hardness of water is measured in terms of ppm (parts per million) of  $\text{CaCO}_3$ . It is the amount (in g) of  $\text{CaCO}_3$  present in  $10^6$  g  $\text{H}_2\text{O}$ . In a sample of water, 10 L

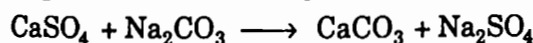
required 0.56 g of CaO to remove temporary hardness of  $\text{HCO}_3^-$



Temporary hardness is

- (a) 200 ppm  $\text{CaCO}_3$       (b) 100 ppm  $\text{CaCO}_3$   
(c) 50 ppm  $\text{CaCO}_3$       (d) 25 ppm  $\text{CaCO}_3$

10. Permanent hardness is due to  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and is removed by the addition of  $\text{Na}_2\text{CO}_3$



If hardness is 100 ppm  $\text{CaCO}_3$ , amount of  $\text{Na}_2\text{CO}_3$  required to soften 10 L of hard water is

- (a) 2.12 g      (b) 0.106 g  
(c) 10.6 g      (d) 1.06 g

11. All the oxygen in a 0.5434-g sample of a pure oxide of iron is removed by reduction in a stream of  $\text{H}_2$ . The loss in weight is 0.1210 g. Hence, formula of the iron oxide is : (Fe = 56)

- (a) FeO      (b)  $\text{Fe}_2\text{O}_3$   
(c)  $\text{Fe}_3\text{O}_4$       (d)  $\text{FeO}_2$

12. A certain sample of phosphate rock contains 26.26%  $\text{P}_2\text{O}_5$ . A 0.5428 g sample is analysed by precipitating  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  and igniting the precipitate to  $\text{Mg}_2\text{P}_2\text{O}_7$ . Thus,  $\text{Mg}_2\text{P}_2\text{O}_7$  obtained is

- (a) 0.8486 g      (b) 0.1424 g  
(c) 0.3648 g      (d) 0.2228 g

13. The calcium in a 0.8432-g sample is precipitated as  $\text{CaC}_2\text{O}_4$ . The precipitate is washed, ignited to  $\text{CaCO}_3$  and found to weigh 0.3462 g. Percentage of CaO in the sample is

- (a) 11.5%      (b) 23%  
(c) 18%      (d) 46%

14. Number of millilitres of a 1.6%  $\text{BaCl}_2$  (w/V) solution which required to precipitate the sulphur as  $\text{BaSO}_4$  in a 0.60-g sample that contains 12% S is

- (a) 58.50 mL      (b) 14.63 mL  
(c) 29.25 mL      (d) 21.00 mL

15. An iron sample contains 18%  $\text{Fe}_3\text{O}_4$ . What is the amount so that it is precipitated as  $\text{Fe}_2\text{O}_3$  which weighs 0.40 g?

- (a) 2.15 g      (b) 1.075 g  
(c) 4.30 g      (d) 2.01 g

16. An aqueous solution of glucose is 10%. The volume in which 1 g mol of it is dissolved will be

- (a) 0.9 L      (b) 9 L  
(c) 1.8 L      (d) 18 L

17. In diammonium phosphate  $(\text{NH}_4)_2\text{HPO}_4$ , the percentage of  $\text{P}_2\text{O}_5$  is

- (a) 35.87      (b) 46.44  
(c) 51.99      (d) 53.78

18. The oxide of an element contains 67.67% of oxygen. Equivalent weight of the element is

- (a) 2.46      (b) 3.82  
(c) 4.36      (d) 4.96

19. Which pair has same percentage of carbon?

- (a)  $\text{CH}_3\text{COOH}$  and  $\text{C}_6\text{H}_{12}\text{O}_6$   
(b)  $\text{CH}_3\text{COOH}$  and  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$   
(c)  $\text{CH}_3\text{COOH}$  and  $\text{C}_2\text{H}_5\text{OH}$   
(d)  $\text{C}_6\text{H}_{12}\text{O}_6$  and  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

20. The mass of 70%  $\text{H}_2\text{SO}_4$  required for neutralization of 1 mole of NaOH is

- (a) 70 g      (b) 35 g  
(c) 30 g      (d) 95 g

21. 1000 g  $\text{CaCO}_3$  solution contain 10 g carbonate. The concentration of solution as carbonate is

- (a) 10 ppm      (b) 100 ppm  
(c) 1000 ppm      (d) 10000 ppm

22. 800 g of a 40% solution by weight was cooled. 100 g of solute precipitated. The percentage composition of remaining solution is

- (a) 31.4%      (b) 20.0%  
(c) 23.0%      (d) 24%

23. The hydrogen phosphate of certain metal has  $\text{MHPO}_4$  formula. The formula of metal chloride is

- (a) MCl      (b)  $\text{M}_2\text{Cl}$   
(c)  $\text{MCl}_3$       (d)  $\text{MCl}_2$

24. A bivalent metal has 37.2 equivalent weight. The molecular weight of its chloride is

- (a) 216.6      (b) 148.8  
(c) 145.4      (d) 172.8

25. A body drinks 500 mL of 9% glucose solution. The number of glucose molecules he has consumed are [mol. wt. of glucose = 180]

- (a)  $0.5 \times 10^{23}$       (b)  $1.0 \times 10^{23}$   
(c)  $1.5 \times 10^{23}$       (d)  $2.0 \times 10^{23}$

### One or More Than One Options Correct

1. 1 mole aqueous solution of  $\text{SO}_2\text{Cl}_2$  is neutralised by

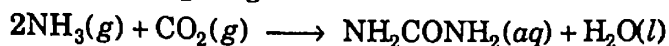
- (a) 2 mol of  $\text{Ca}(\text{OH})_2$       (b) 1 mol of  $\text{Ca}(\text{OH})_2$   
(c) 2 mol KOH      (d) 4 mol KOH

2. The molar mass of haemoglobin is about  $65000 \text{ g mol}^{-1}$ . Every haemoglobin contains 4 iron atoms. Thus

- (a) iron content in haemoglobin is 0.35% by mass  
(b) 1 mole of haemoglobin contains 56 g iron  
(c) 1 mole of haemoglobin contains 224 g iron  
(d) if iron content is increased to 0.56%, molar mass of haemoglobin would be higher than  $65000 \text{ g mol}^{-1}$ .



3. In one process giving below



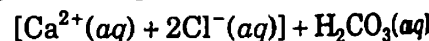
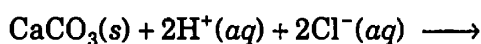
637.2 g of  $\text{NH}_3$  are allowed to react with 1142 g of  $\text{CO}_2$ . In this

- $\text{NH}_3$  is the limiting reactant and  $\text{CO}_2$  is in excess
  - $\text{NH}_3$  is in excess and  $\text{CO}_2$  is the limiting reactant
  - 1124 g of urea is formed
  - 319 g of  $\text{CO}_2$  is left unreacted
4. If 0.80 mole of  $\text{MnO}_2$  and 146 g of  $\text{HCl}$  react
- $$\text{MnO}_2 + 4\text{HCl} \longrightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$$
- then,
- 0.80 mole of  $\text{Cl}_2$  is formed
  - 0.80 mole of  $\text{HCl}$  remains unreacted
  - $\text{MnO}_2$  is completely reacts
  - $\text{MnO}_2$  is the limiting reactant
5. When 0.273 g of  $\text{Mg}$  is heated strongly in a nitrogen ( $\text{N}_2$ ) atmosphere, a chemical reaction occurs. The product of the reaction weighs 0.378 g. Empirical formula of the compound
- $\text{MgN}$
  - $\text{Mg}_3\text{N}_2$
  - $\text{MgN}_2$
  - $\text{Mg}_2\text{N}$
6. We have 1.6 g  $\text{CH}_4$ , 1.7 g  $\text{NH}_3$  and 1.8 g  $\text{H}_2\text{O}$  select correct alternate(s)
- There are equal number of moles of each reactant
  - Total number of atoms in  $\text{CH}_4 > \text{NH}_3 > \text{H}_2\text{O}$
  - Total number of H-atoms are in the ratio of 4 : 3 : 2
  - Total number of C-atoms in  $\text{CH}_4 <$  that of N-atoms in  $\text{NH}_3 <$  that of O-atoms in  $\text{H}_2\text{O}$
7. Density of  $\text{H}_2\text{O}$  is  $1 \text{ g mL}^{-1}$ . If we have 1 mL  $\text{H}_2\text{O}$  then
- it is  $55.55 \text{ mol L}^{-1}$
  - it has  $3.33 \times 10^{22}$   $\text{H}_2\text{O}$  molecules
  - it has  $3.33 \times 10^{22}$  H-atoms
  - it has  $6.66 \times 10^{22}$  O-atoms
8. In diammonium hydrogen phosphate,  $(\text{NH}_4)_2\text{HPO}_4$ , percentage as
- $\text{P}_2\text{O}_5$  is 53.78%
  - $\text{NH}_3$  is 25.76%
  - P is maximum
  - N is maximum
9. Mole fraction of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) is ethanol-water system is 0.25. Thus it has
- 25% ethanol by weight of solution
  - 75% water by weight of solution
  - 46% ethanol by weight of solution
  - 54% water by weight of solution
10. 12.8 g of mixture of  $\text{MCl}$  (volatile) and  $\text{KCl}$  (non-volatile) on reaction with excess of aqueous  $\text{AgNO}_3$  solution gave 28.7 g white precipitate. 12.8 g of same mixture on a heating gave a gas that on passing into

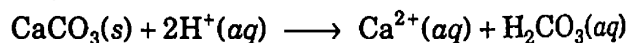
$\text{AgNO}_3$  solution gave 14.35 g of white precipitate. Hence,

- ionic mass of  $\text{M}^+$  is  $18 \text{ g mol}^{-1}$
- mixture has equal mole fraction of  $\text{MCl}$  and  $\text{KCl}$
- $\text{KCl}$  and  $\text{MCl}$  when separately treated with  $\text{AgNO}_3$  solution would give same number of moles of white precipitates
- $\text{AgCl}$  is water soluble

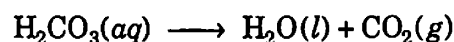
## Brain Twisters



Thus, net reaction is



This is an exothermic reaction (in which heat is evolved) and thus there is thermal decomposition of carbonic acid into gaseous carbon dioxide and water. Explain



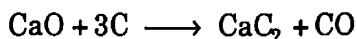
2. For each of the following write balanced

- formulae unit
- total ionic, and
- net ionic equations

(Refer Table 6.1)

- Black-and-white photographic film contains some silver bromide, which can be formed by the reaction of sodium bromide with silver nitrate.
  - Barium sulphate is used when X-rays of gastrointestinal tract are made. It can be prepared by reacting barium chloride with dilute sulphuric acid.
  - In water purification, small solid particles are often "trapped" as aluminium hydroxide precipitates and falls to the bottom of the sedimentation pool. Aluminium sulphate reacts with calcium hydroxide (from lime) to form aluminium hydroxide and calcium sulphate. (Do not use  $\text{NaOH}$ , why?)
  - Our bones are mostly calcium phosphate. Calcium chloride reacts with potassium phosphate to form calcium phosphate and calcium sulphate.
3. Aluminium building materials have a hard transparent protective coating of aluminium oxide, formed by reaction with oxygen in air. The sulphuric acid,  $\text{H}_2\text{SO}_4$ , in acid rain dissolves this protective coating and forms aluminium sulphate and water.
- How many moles of  $\text{H}_2\text{SO}_4$  are required to react with 4.0 moles of  $\text{Al}_2\text{O}_3$ ?
  - How many moles of  $\text{Al}_2(\text{SO}_4)_3$  are formed in (a)

4. Calcium carbide is made in an electric furnace by the reaction.



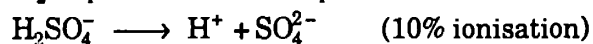
The crude product is usually 85%  $\text{CaC}_2$  and 15% unreacted  $\text{CaO}$ .

- (a) How much  $\text{CaO}$  should we start with to produce 450 kg of crude product
- (b) How much  $\text{CaC}_2$  would this crude product contain?
5. A mixture of  $\text{CuSO}_4$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  has a mass of 1.245 g. After heating to drive off all the water, the mass is only 0.832 g. What is the mass per cent of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in the mixture?
6. Nickel forms a compound with carbon monoxide,  $\text{Ni}_x(\text{CO})_y$ . To determine its formula, you carefully heat a 0.0973 g sample in air to convert the nickel to 0.0426 g of  $\text{NiO}$  and the  $\text{CO}$  to 0.100 g  $\text{CO}_2$ . What is the empirical formulae of  $\text{Ni}_x(\text{CO})_y$  [ $\text{Ni} = 58.7$ ]
7. Sodium azide, the explosive chemical used in automobile airbags, is made by the following reaction.
- $$\text{NaNO}_3 + 3\text{NaNH}_2 \longrightarrow \text{NaN}_3 + 3\text{NaOH} + \text{NH}_3$$
- If you combine 15.0 g  $\text{NaNO}_3$  with 15.0 g  $\text{NaNH}_2$ , what mass of  $\text{NaN}_3$  is produced?
8. Silicon and hydrogen form a series of compounds with general formula  $\text{Si}_x\text{H}_y$ . A 6.22 g sample of the compound is burnt in oxygen. All the  $\text{Si}$  is converted to 11.64 g of  $\text{SiO}_2$ , and all of the  $\text{H}$  is converted to 6.980 g of  $\text{H}_2\text{O}$ . What is the empirical formula of the silicon compound? ( $\text{Si} = 28$ )
9. Copper metal can be prepared from copper ore in following steps :
- I:  $\text{Cu}_2\text{S}(s) + \text{O}_2(g) \longrightarrow 2\text{Cu}(s) + \text{SO}_2(g)$
- II:  $\text{CuS}(s) + \text{O}_2(g) \longrightarrow \text{Cu}(s) + \text{SO}_2(g)$
- Suppose an ore sample contains 11.0% impurity in addition to a mixture of  $\text{CuS}$  and  $\text{Cu}_2\text{S}$ . Heating 100.0 g of the mixture produces 75.4 g of copper metal with a purity of 89.5% what is the weight per cent of  $\text{CuS}$  and  $\text{Cu}_2\text{S}$  in the ore?
10. In some countries, a person will receive a "driving while intoxicated" (DWI) ticket if the blood alcohol level (BAL) is 100 mg per decilitre (dL) of blood or higher. Suppose a person is found to have a BAL of 0.033 mole of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) per litre of blood. Will a person receive a DWI ticket?

## Passage Comprehension Questions

### Passage 1

When sulphuric acid dissolves in water, the following reactions take place



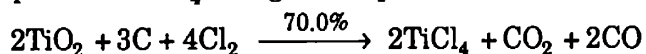
We start with 0.2 M aqueous solution of  $\text{H}_2\text{SO}_4$ .

Answer the following questions.

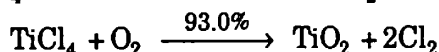
- $[\text{SO}_4^{2-}]$  in the above case is
  - 0.1 M
  - 0.01 M
  - 0.2 M
  - 0.02 M
- $[\text{HSO}_4^-]$  in the above case is
  - 0.1 M
  - 0.09 M
  - 0.18 M
  - 0.08 M
- $[\text{H}_3\text{O}^+]$  in aqueous solution is
  - 0.28 M
  - 0.22 M
  - 0.02 M
  - 0.10 M
- Maximum concentration is species
  - $\text{H}_2\text{SO}_4$
  - $\text{H}_3\text{O}^+$
  - $\text{SO}_4^{2-}$
  - $\text{HSO}_4^-$

### Passage 2

About half of the world's production of pigments for paints involves the formation of white  $\text{TiO}_2$ . In the United States, it is made on a large scale by the chloride process, starting with ores containing only small amounts of rutile,  $\text{TiO}_2$ . The ore is treated with chlorine and carbon (coke). This produces  $\text{TiCl}_4$  and gaseous products.



The  $\text{TiCl}_4$  is then converted into  $\text{TiO}_2$  of high purity.



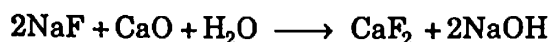
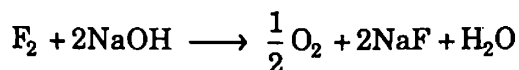
Efficiencies have been indicated above the arrow mark. ( $\text{Ti} = 48$ ,  $\text{Cl} = 35.5$ ,  $\text{O} = 16$ ,  $\text{C} = 12$ )

Answer the following questions

- If we start with 100 kg of ore (containing 7.5% rutile), pure  $\text{TiO}_2$  obtained is
  - 4.8825 kg
  - 7.3238 kg
  - 9.7650 kg
  - 2.4413 kg
- $\text{Cl}_2$  required in this reaction is
  - 0.1221 kmol
  - 8.666 kg
  - 4.333 kg
  - 0.1221 kg

### Passage 3

A fluorine disposal plant was constructed to carry out the reactions



As the plant operated, excess lime was added to bring about complete precipitation of the fluoride as  $\text{CaF}_2$ . Over a period of operation, 2000 kg of fluorine were fed into a plant and 10,000 kg of lime were required. (F = 19, Ca = 40, O = 16, H = 1, Na = 23)

Answer the following questions

- What was the percentage utilisation of lime ( $\text{CaO}$ )?
  - 29.5%
  - 14.75%
  - 59.0%
  - 60.0%
- $\text{CaO}$  used by given quantity of  $\text{F}_2$  is
  - 1475 kg
  - 2947.4 kg
  - 5900 kg
  - 6000 kg
- $\text{CaF}_2$  precipitated is
  - 37.79 kmol
  - 263.16 kmol
  - 35.71 kmol
  - 26.32 kmol

### Passage 4

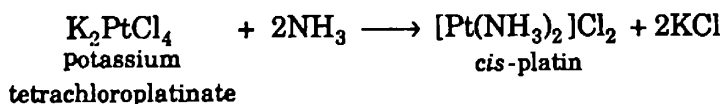
11.2 g of mixture of  $\text{MCl}$  (volatile) and  $\text{NaCl}$  gave 28.7 g of white precipitate with excess of  $\text{AgNO}_3$  solution. 11.2 g of same mixture on heating gave a gas that on passing into  $\text{AgNO}_3$  solution gave 14.35 g of white precipitate

Answer the following questions

- Ionic mass of  $\text{M}^+$  is
  - 18
  - 9
  - 36
  - 23
- $\text{MCl}$  and  $\text{NaCl}$  are the molar ratio
  - 1:1
  - 1:2
  - 2:1
  - 1:3
- In terms of moles, mixture has
  - 0.2 mol
  - 0.1 mol
  - 0.15 mol
  - 0.01 mol

### Passage 5

Cisplatin, an anticancer agent used for the treatment of solid tumors, is prepared by the reaction of ammonia with potassium tetra chloroplatinate



Assume that 10.0 g of  $\text{K}_2\text{PtCl}_4$  and 10.0 of  $\text{NH}_3$  are allowed to react. (K = 39, Pt = 195, Cl = 35.5)

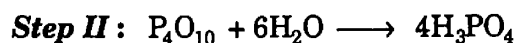
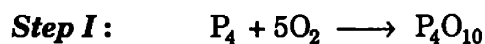
Answer the following questions

- Which reactant is limiting and which is in excess?
 

| Limiting                                                   | Excess                    |
|------------------------------------------------------------|---------------------------|
| (a) $\text{K}_2\text{PtCl}_4$                              | $\text{NH}_3$             |
| (b) $\text{NH}_3$                                          | $\text{K}_2\text{PtCl}_4$ |
| (c) Exact molar ratio                                      |                           |
| (d) Would be decided by the quantity of the product formed |                           |
- Number of moles of  $\text{K}_2\text{PtCl}_6$  consumed is
  - 0.048
  - 0.024
  - 0.012
  - 0.096
- Number of moles of  $\text{NH}_3$  consumed is
  - 0.048
  - 0.024
  - 0.096
  - 0.192
- Number of moles of *cis*-platin formed is
  - 0.012
  - 0.024
  - 0.048
  - 0.192
- Number of moles of excess reactant which remains unreacted is
  - 0.024
  - 0.34
  - 0.54
  - 0.56

### Passage 6

Phosphoric acid,  $\text{H}_3\text{PO}_4$ , is widely used to make fertilisers, and can be prepared in a two-step process.



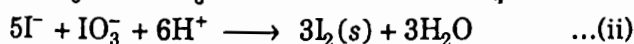
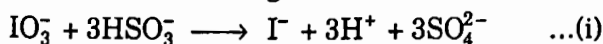
We allow 310 g of phosphorus to react with excess oxygen, which forms tetraphosphorus decoxide,  $\text{P}_4\text{O}_{10}$ , in 50% yield. In the step II reaction, 25% yield of  $\text{H}_3\text{PO}_4$  is obtained. (P = 31, H = 1, O = 16)

Answer the following questions

- Assume 100% yield then number of moles of  $\text{H}_3\text{PO}_4$  would be obtained
  - 1.25
  - 10.0
  - 5.0
  - 2.5
- Actual number of moles of  $\text{H}_3\text{PO}_4$  obtained based on experimental conditions is
  - 5.0
  - 2.5
  - 1.25
  - 0.3125
- $\text{H}_3\text{PO}_4$  thus formed is converted into calcium phosphate by treating with 1 mole of calcium hydroxide. Calcium phosphate obtained is
  - 2.5
  - 0.33
  - 0.1563
  - 1.25

### Passage 7

Chile salt peter is a natural source of  $\text{NaNO}_3$  which also contains  $\text{NaIO}_3$ . The  $\text{NaIO}_3$  can be used as a source of iodine produced in the following reactions



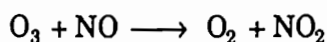
1.00 L of the starting solution which contains 5.80 g  $\text{NaIO}_3/\text{L}$ , is treated with stoichiometric quantity of  $\text{NaHSO}_3$ . Then a further quantity of the starting solution is added to the reaction mixture to bring about the second reaction. [I = 127, Na = 23, S = 32]

Answer the following questions

- How many grams of  $\text{NaHSO}_3$  are required in step (i)?  
(a) 5.80 g (b) 17.4 g  
(c) 9.14 g (d) 3.0 g
- What additional volume of the starting solution must be added in step (ii)?  
(a) 0.2 L (b) 0.4 L  
(c) 0.8 L (d) 1.0 L
- How many equivalents of  $\text{IO}_3^-$  are present in one mole of  $\text{NaIO}_3$  in step (i)?  
(a) 2 (b) 4  
(c) 6 (d) 8
- How many equivalents of  $\text{IO}_3^-$  are used in step (ii)?  
(a) 6 (b) 5  
(c) 0.06 (d) 0.035

### Passage 8

The depletion of ozone ( $\text{O}_3$ ) in the stratosphere has been a matter of great concern among scientists in recent years. It believed that ozone can react with nitric oxide (NO) that is discharged from the high altitude jet plane. The reaction is

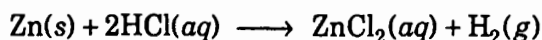


Answer the following questions

- If 0.740 g of  $\text{O}_3$  reacts with 0.670 g of NO, how many gram of  $\text{NO}_2$  will be produced?  
(a) 0.71 g (b) 0.74 g  
(c) 0.68 g (d) 0.81 g
- Which compound is the limiting reactant?  
(a) NO  
(b)  $\text{O}_3$   
(c) Both are in equimolar ratio  
(d) Both are in stoichiometric ratio
- Number of moles of the excess reactant remaining at the end of the reaction is  
(a) 0.007 mol  $\text{O}_3$  (b) 0.014 mol  $\text{O}_3$   
(c) 0.007 mol NO (d) 0.014 mol NO

### Passage 9

Let us explore a reaction with a limiting reactant. Here zinc metal is added to a flask containing aqueous HCl and  $\text{H}_2$  gas is a product

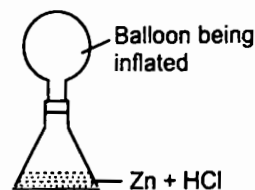


Each of three flasks contain 0.10 mol HCl. Zinc is added to each flask in the following quantities :

Flask 1 : 7.00 g Zn

Flask 2 : 3.27 g Zn

Flask 3 : 1.31 g Zn



When the reactants are combined, the  $\text{H}_2$  inflates the balloon attached to the flask.

Based on the above experiment, answer the following questions

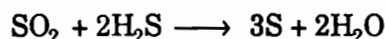
- Balloon is inflated completely in  
(a) flask 1 (b) flask 2  
(c) Both (a) and (b) (d) None of these
- Zinc reacts completely in  
(a) flask 1 (b) flask 2  
(c) flask 3 (d) flask 2 and 3
- Consider following statements  
I : In flask 1, balloon inflates completely, but some Zn remains when inflation ceases  
II : In flask 2, balloon inflates completely, but no Zn remains  
III : In flask 3, balloon does not inflate completely and no zinc remains  
Select correct statements.  
(a) I, II, III (b) I, II  
(c) I, III (d) II, III

### Assertion & Reason

Codes :

- Both **A** and **R** are true and **R** is the correct explanation of **A**.
- Both **A** and **R** are true but **R** is not the correct explanation of **A**.
- A** is true but **R** is false.
- A** is false but **R** is true.

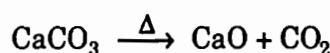
- Assertion (A) :** In the following reaction



1 mole  $\text{SO}_2$  and 1 mole  $\text{H}_2\text{S}$  form 3 moles sulphur.

**Reason (R) :** 1 mole  $\text{SO}_2$  and 2 moles  $\text{H}_2\text{S}$  form 3 moles sulphur and 2 moles  $\text{H}_2\text{O}$ .

- Assertion (A) :** 20 g of 50% pure  $\text{CaCO}_3$  on heating gave 2.24 L  $\text{CO}_2$  at STP and 15.6 g non-volatile residue.



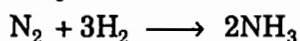
**Reason (R) :** Pure  $\text{CaCO}_3$  is 10 g which gave 4.4 g  $\text{CO}_2$  ( $= 0.1 \text{ mol} = 2.24 \text{ L}$  at STP) and 15.6 g residue is left.

3. **Assertion (A) :**  $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$

2 g  $\text{H}_2$  react with 1 g  $\text{O}_2$  to form 2 g  $\text{H}_2\text{O}$ .

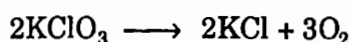
**Reason (R) :** 2 moles  $\text{H}_2$  react with 1 mole  $\text{O}_2$  to form 2 moles  $\text{H}_2\text{O}$ .

4. **Assertion (A) :** 2 moles  $\text{N}_2$  react with 3 moles  $\text{H}_2$  to form 2 moles  $\text{NH}_3$ .



**Reason (R) :**  $\text{N}_2$  is excess and  $\text{H}_2$  is the limiting reactant.

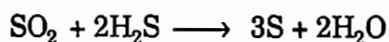
5. **Assertion (A) :** 4 moles of  $\text{KClO}_3$  (50% pure) gave 3 moles of  $\text{O}_2$  on heating strongly and thus yield is 100%



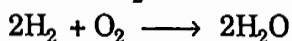
**Reason (R) :** 3 moles of  $\text{O}_2$  are obtained from 2 moles of  $\text{KClO}_3$ .

## True & False

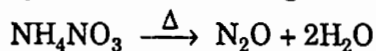
- 1 mole of  $\text{Ag}_2\text{CO}_3$  on strongly heating gave 1 mole of residue.
- 1 mole of  $\text{Na}_2\text{CO}_3$  and 2 moles of  $\text{NaHCO}_3$  on heating gave 2 moles residue, 1 mole  $\text{CO}_2$  and 1 mole  $\text{H}_2\text{O}$ .
- 1 mole  $\text{SO}_2$  and 1 mole  $\text{H}_2\text{S}$  form 3 moles S.



4. In the reaction between 2 g  $\text{H}_2$  and 3 g  $\text{O}_2$ ,  $\text{H}_2$  is the limiting reactant and  $\text{O}_2$  is in excess.



5. Percentage yield in the following reaction is 50%.



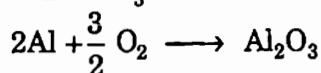
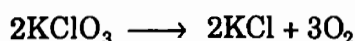
1 mole of 50% pure  $\text{NH}_4\text{NO}_3$  gave 11.2 L  $\text{N}_2\text{O}$  at STP.

6. 100 mL of 20.8%  $\text{BaCl}_2$  (molar mass = 208) and 50 mL of 17.4%  $\text{K}_2\text{SO}_4$  (molar mass = 174) form 0.5 moles of  $\text{BaSO}_4$  (molar mass = 233)

7. 1 g  $\text{AgNO}_3$  reacts with 1 g  $\text{HCl}$  to form 1 g  $\text{AgCl}$ .

8. 2 moles of  $\text{PCl}_5$  are 50% dissociated at 400 K. After reaction, there are total of 3 moles.

9. In the following reactions,



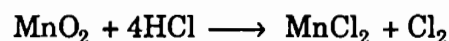
1 mole of  $\text{KClO}_3$  is required to form 1 mole  $\text{Al}_2\text{O}_3$ .

10. Gravimetry is studied under stoichiometry.

## Fill in the Blanks

1. 16.8 g of mixture of  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  (50% each) on strongly heating gives ..... L  $\text{CO}_2$  at STP.

2. In the following reaction,



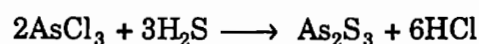
1 mole each of  $\text{MnO}_2$  and  $\text{HCl}$  forms ..... g  $\text{Cl}_2$ .

3.  $\text{C(s)} + \text{H}_2\text{O} \longrightarrow \text{CO} + \text{H}_2$



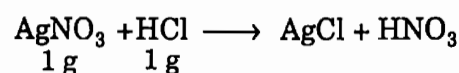
To prepare 1 mole of  $\text{Ni(CO)}_4$ ,  $\text{C(s)}$  required is ..... mole.

4. In the reaction between 1 mole each of  $\text{H}_2\text{S}$  and  $\text{AsCl}_3$ .



limiting reagent is .....

5. In the following reaction,



unreacted reagent is .....

## Matrix-Match Type Questions

### I. Only One Correct

1. Match the number of moles (in List I) with the compound (in List II).

| List I     | List II                                   |
|------------|-------------------------------------------|
| A. 0.5 mol | 1. 92 g $\text{CH}_3\text{CH}_2\text{OH}$ |
| B. 1.0 mol | 2. 66 g $\text{CO}_2$                     |
| C. 1.5 mol | 3. 54 g $\text{H}_2\text{O}$              |
| D. 2.0 mol | 4. 15 g $\text{HCHO}$                     |
| E. 3.0 mol | 5. 44 g $\text{CH}_3\text{CHO}$           |

2. Match the reaction (in List I) with the maximum yield of the product (in List II).

| List I                                                                                                                              | List II    |
|-------------------------------------------------------------------------------------------------------------------------------------|------------|
| A. $\begin{array}{ccc} 2\text{H}_2 + \text{O}_2 & \longrightarrow & 2\text{H}_2\text{O} \\ 1 \text{ g} & 1 \text{ g} & \end{array}$ | 1. 1.028 g |
| B. $\begin{array}{ccc} 3\text{H}_2 + \text{N}_2 & \longrightarrow & 2\text{NH}_3 \\ 1 \text{ g} & 1 \text{ g} & \end{array}$        | 2. 1.333 g |
| C. $\begin{array}{ccc} \text{H}_2 + \text{Cl}_2 & \longrightarrow & 2\text{HCl} \\ 1 \text{ g} & 1 \text{ g} & \end{array}$         | 3. 1.125 g |
| D. $\begin{array}{ccc} 2\text{H}_2 + \text{C} & \longrightarrow & \text{CH}_4 \\ 1 \text{ g} & 1 \text{ g} & \end{array}$           | 4. 1.214 g |

## II. One or More Correct

1. Match Column I (reactant) with the amount in Column II.

| Column I                                                                                                                                                                            | Column II        |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|
| A. $\text{CH}_3\text{COOH} + \text{NaOH} \longrightarrow$<br>1 mol<br>$\text{CH}_3\text{COONa} + \text{H}_2\text{O}$<br>NaOH used to react completely with $\text{CH}_3\text{COOH}$ | 1. 1 mole        |
| B. $\text{MgCO}_3 \xrightarrow{\Delta} \text{MgO} + \text{CO}_2$<br>84 g<br>Residue formed                                                                                          | 2. 1 equivalent  |
| C. $2\text{SO}_2 + \text{O}_2 \longrightarrow 2\text{SO}_3$<br>2 mol 64 g<br>Reactant in excess under standard conditions                                                           | 3. 40 g          |
| D. $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$<br>$\text{O}_2$ used to form 36 g $\text{H}_2\text{O}$                                                            | 4. 22.4 L at STP |
| E. $\text{N}_2\text{H}_4 + \text{O}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$<br>$\text{N}_2$ formed from 32 g each reactant                                              | 5. 4 equivalents |

## Integer Answer Types

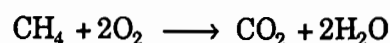
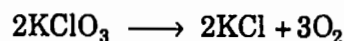
This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the ORS have to be darkened. For example, if the correct answers to question number X, Y, Z and W (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will like the following

| X                       | Y                       | Z                       | W                       |
|-------------------------|-------------------------|-------------------------|-------------------------|
| <input type="radio"/> 0 | <input type="radio"/> 0 | <input type="radio"/> 0 | <input type="radio"/> 0 |
| <input type="radio"/> 1 | <input type="radio"/> 1 | <input type="radio"/> 1 | <input type="radio"/> 1 |
| <input type="radio"/> 2 | <input type="radio"/> 2 | <input type="radio"/> 2 | <input type="radio"/> 2 |
| <input type="radio"/> 3 | <input type="radio"/> 3 | <input type="radio"/> 3 | <input type="radio"/> 3 |
| <input type="radio"/> 4 | <input type="radio"/> 4 | <input type="radio"/> 4 | <input type="radio"/> 4 |
| <input type="radio"/> 5 | <input type="radio"/> 5 | <input type="radio"/> 5 | <input type="radio"/> 5 |
| <input type="radio"/> 6 | <input type="radio"/> 6 | <input type="radio"/> 6 | <input type="radio"/> 6 |
| <input type="radio"/> 7 | <input type="radio"/> 7 | <input type="radio"/> 7 | <input type="radio"/> 7 |
| <input type="radio"/> 8 | <input type="radio"/> 8 | <input type="radio"/> 8 | <input type="radio"/> 8 |
| <input type="radio"/> 9 | <input type="radio"/> 9 | <input type="radio"/> 9 | <input type="radio"/> 9 |

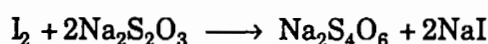
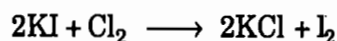
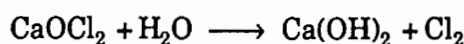
## Set I

- What mass (in grams) of  $\text{CH}_4$  produces  $3.01 \times 10^{23}$   $\text{H}_2\text{O}$  molecules when burnt to excess  $\text{O}_2$ ?
- How many moles of  $\text{H}_2\text{O}$  are formed by 10 moles of  $\text{HNO}_3$  and 10 moles  $\text{Cu}$  in the following reaction?  
 $3\text{Cu} + 8\text{HNO}_3 \longrightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
- 20.8 g of  $\text{MCl}_x$  ( $M = 137$ ) or reaction with excess of  $\text{K}_2\text{SO}_4$  yields 23.3 g of sulphate of metal  $M$ . Calculate value of  $x$ .
- Free  $\text{SO}_3$  in one mole of pure oleum is ..... mole.
- The molar mass of haemoglobin is about  $65000 \text{ g mol}^{-1}$ . Haemoglobin contains 0.35% Fe by mass. Thus, iron atoms present in haemoglobin molecules are .....
- How many moles of oxygen are required to react completely with 24 g of  $\text{CH}_4$ ?

- How many moles of  $\text{KClO}_3$  would be required to supply the proper amount of oxygen needed to burn 24 g of  $\text{CH}_4$  completely?



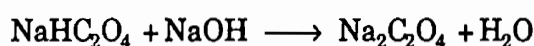
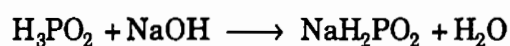
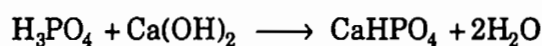
8. In the following sequence of reactions



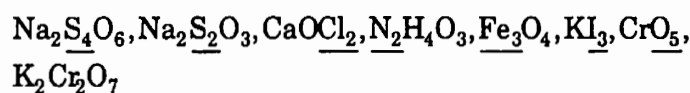
Calculate moles of  $\text{Na}_2\text{S}_2\text{O}_3$  required for complete reduction of  $\text{I}_2$  obtained from 127 g  $\text{CaOCl}_2$  sample (50% purity).

## Set II

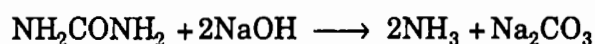
- How many species form 0.05 mole from 3 g of  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{NH}_2\text{CONH}_2$ ,  $\text{HNO}_3$ ?
- How many substances underlined have equivalent weight equal to molecular weight based on the reactions?



- 1 mole of  $\text{C}_2\text{H}_x$  is oxidised to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  by 3 moles  $\text{O}_2$ . Thus, 140 g  $\text{C}_2\text{H}_x$  has ..... moles.
- Out of the following, how many substances have underlined atoms of different nature?



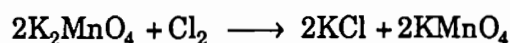
- 6 g urea sample on heating with  $\text{NaOH}$  give 0.224 L  $\text{NH}_3$  at STP.



Thus, percentage yield of  $\text{NH}_3$  is .....

- Sample of  $\text{CaCO}_3$  of 50% purity forms 0.56 g residue. Thus, sample weighs ..... g.
- Pure nitrogen is obtained by decomposition of nitride  $\text{M}_x(\text{N}_3)_y$  where  $x + y = ?$

8. In the following reaction

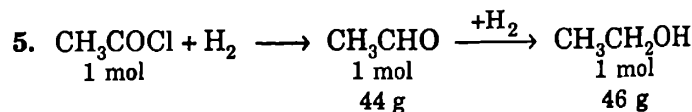


2 moles  $\text{Cl}_2$  and 2 moles  $\text{K}_2\text{MnO}_4$  form ..... moles  $\text{KMnO}_4$ .

# Answers & Solutions

## Numerical Problems Solving

- $2\text{KClO}_3(s) \longrightarrow 2\text{KCl}(s) + 3\text{O}_2(g)$
  - $\text{P}_4(s) + 5\text{O}_2(g) \longrightarrow \text{P}_4\text{O}_{10}(s)$
  - $\text{Zn}(s) + 4\text{HNO}_3(aq) \longrightarrow \text{Zn}(\text{NO}_3)_2(aq) + 2\text{NO}_2(g) + 2\text{H}_2\text{O}(l)$
  - $2\text{Al}(s) + 2\text{NaOH}(aq) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{NaAlO}_2(aq) + 3\text{H}_2(g)$
- $\text{CH}_3\text{COOH}(aq) + \text{NH}_4\text{OH}(aq) \longrightarrow \text{CH}_3\text{COO}^-(aq) + \text{NH}_4^+(aq) + \text{H}_2\text{O}(l)$
- $\text{CrO}_4^{2-}(aq) + 2\text{Ag}^+(aq) \longrightarrow \text{Ag}_2\text{CrO}_4(s)$
  - $\text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \longrightarrow \text{BaSO}_4(s)$
  - $\text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) \longrightarrow \text{CaCO}_3(s)$
- 2 mol  $\text{NH}_3$
  - 2 mol,  $\text{N}_2$  is in excess
  - 2.66 mol,  $\text{N}_2$  is in excess
  - 0.66 mol,  $\text{H}_2$  is limiting reagent.



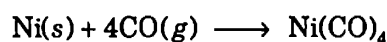
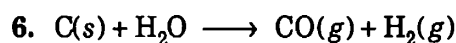
If no side reaction,  $\text{CH}_3\text{CHO} = 44 \text{ g}$

but same  $\text{CH}_3\text{CH}_2\text{OH}$  is also formed.

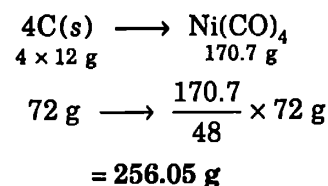
$\text{CH}_3\text{CH}_2\text{OH} = 2.3 \text{ g}$  for  $4.4 \text{ g}$   $\text{CH}_3\text{CHO}$

Thus, actual yield of  $\text{CH}_3\text{CHO} = 44.0 - 4.4 = 39.6 \text{ g}$

$$\% \text{ yield} = \frac{39.6}{44.0} \times 100 = 90.0\%$$



After balancing



## Master Exercises

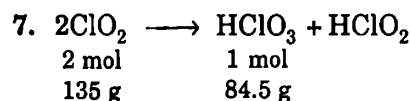
### Exercise 1

#### Short Answer Type Questions

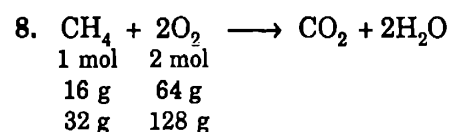
- Soluble :  $\text{NaOH}$ ,  $\text{CaO}$   
Partial soluble :  $\text{CaSO}_4$   
Insoluble :  $\text{FeS}$ ,  $\text{PbS}$ ,  $\text{CaCO}_3$ ,  $\text{CaC}_2\text{O}_4$
- Interaction between cation and anion that leads to formation of insoluble salts
- $\text{H}^+(aq) + \text{OH}^-(aq) \longrightarrow \text{H}_2\text{O}(aq)$
- $$\begin{array}{ccc} \text{HCl}(aq) + \text{NaOH}(aq) & \longrightarrow & \text{NaCl}(aq) + \text{H}_2\text{O} \\ 1 \text{ mol} & 1 \text{ mol} & \\ \\ 2\text{HCl}(aq) + \text{Ca}(\text{OH})_2(aq) & \longrightarrow & \text{CaCl}_2(aq) + 2\text{H}_2\text{O} \\ 2 \text{ mol} & 1 \text{ mol} & \\ 1 \text{ mol} & 0.5 \text{ mol} & \end{array}$$
- $$\begin{array}{ccc} \text{Ca}(\text{OH})_2 + \text{H}_2\text{SO}_4 & \longrightarrow & \text{CaSO}_4 + 2\text{H}_2\text{O} \\ 1 \text{ mol} & 1 \text{ mol} & \\ \\ 2\text{KOH} + \text{H}_2\text{SO}_4 & \longrightarrow & \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O} \\ 2 \text{ mol} & 1 \text{ mol} & \\ 1 \text{ mol} & 0.5 \text{ mol} & \end{array}$$

- $\text{NO} = 10 \text{ moles}$

$\text{NOBr} = 10 \text{ moles}$



$$8.36 \text{ kg HClO}_3 \text{ is from} = \frac{135}{84.5} \times 8.36 \text{ CO}_2 = 13.356 \text{ kg ClO}_2$$

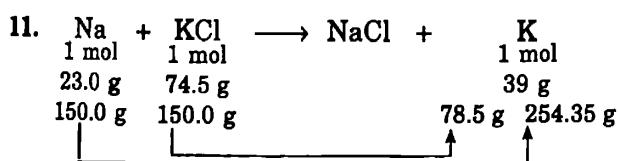
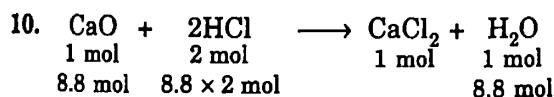


- $$\begin{array}{ccc} \text{C}_5\text{H}_{12}(g) + 8\text{O}_2(g) & \longrightarrow & 5\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \\ 1 \text{ mol} & 5 \text{ mol} & \\ 1 \text{ mole} = 72 \text{ g} & 5 N_0 \text{ molecules} & \end{array}$$

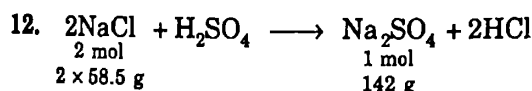
$5 \times 6.02 \times 10^{23}$  molecules of  $\text{CO}_2$  are from  $= 72 \text{ g C}_5\text{H}_{12}$

Thus,  $3.01 \times 10^{22}$  molecules of  $\text{CO}_2$  are from

$$= \frac{72 \times 3.01 \times 10^{22}}{5 \times 6.02 \times 10^{23}} = 0.72 \text{ g C}_5\text{H}_{12}$$



KCl is a limiting quantity and thus, K formed = 78.5 g



117 g NaCl yield = 142 g pure  $\text{Na}_2\text{SO}_4$

$$\left(245 \times \frac{93.9}{100}\right) \text{ g NaCl yield} = \frac{142 \times 245 \times 93.9}{117 \times 100} \text{ g}$$

pure  $\text{Na}_2\text{SO}_4$

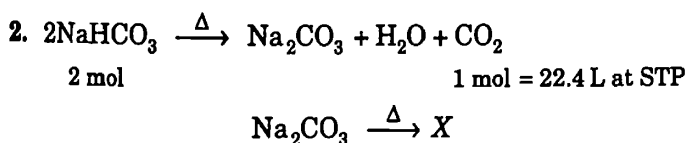
$$= 279.21 \text{ g pure } \text{Na}_2\text{SO}_4$$

$$= 279.21 \times \frac{100}{74.1} \text{ of } 74.1\% \text{ purity}$$

$$= 376.80 \text{ g}$$

## Analytical Questions

1. 4236 g



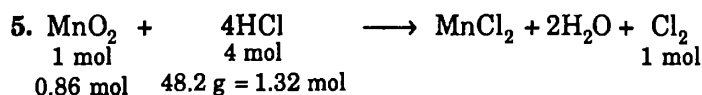
$$\text{NaHCO}_3 \text{ in mixture} = 4 \times \frac{75}{100} = 3 \text{ g} = 0.0357 \text{ mol}$$

$$\text{CO}_2 \text{ formed} = \frac{0.0357}{2} \text{ mol}$$

$$= \frac{0.0357}{2} \times 22.4 \text{ L CO}_2 \text{ at STP}$$

$$= 0.4 \text{ L} = 400 \text{ mL}$$

3. 5.943 L    4. 41 kg  $\text{H}_2\text{O}$ ,  $\text{Li}_2\text{O}$  is limiting reactant



HCl required by 0.86 mol  $\text{MnO}_2$  = 3.44 mol

but HCl taken = 1.32 mol

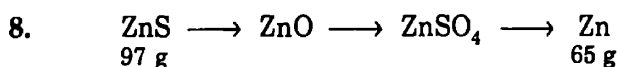
Thus, HCl is the limiting reactant.

$$\text{Thus, } \text{Cl}_2 \text{ formed} = \frac{1}{4} \times 1.32$$

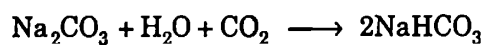
$$= 0.33 \text{ mol Cl}_2$$

$$= 23.43 \text{ g}$$

6. 29.80%    7. (a) 863.08 g (b) 93.04%



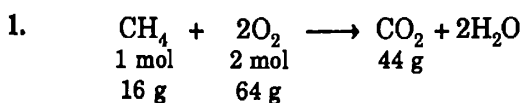
$$\therefore \frac{225 \times 90.6 \times 100 \times 98.2}{100 \times 100 \times 100} \text{ kg gives Zn} = 134.14 \text{ kg}$$



$$50 \text{ g}$$

## Exercise 2

### Only One Option Correct



given 16 g 48 g = 1.5 mol

Thus,  $\text{O}_2$  is the limiting reactant

$$\therefore 2 \text{ mol O}_2 \text{ give} = 44 \text{ g CO}_2$$

$$1.5 \text{ mol O}_2 \text{ give} = \frac{44}{2} \times 1.5 = 33 \text{ g CO}_2$$

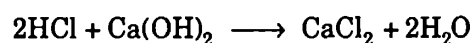
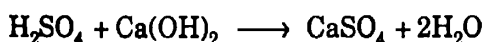
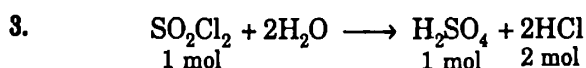
Thus, (b)

2. Ratio of  $\text{HNO}_3$  per mol of  $\text{H}_2\text{O}$

(a)  $\frac{8}{4} = 2$                       (b)  $\frac{6}{3} = 2$

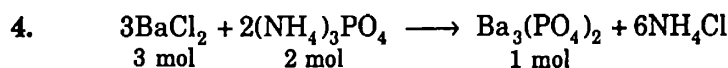
(c)  $\frac{10}{3} = 3.33$                       (d)  $\frac{4}{2} = 2$

Thus, (c)



Thus, total  $\text{Ca(OH)}_2$  required = 2 mol

Thus, (a)



given 0.5 mol                      0.2 mol                      0.1 mol

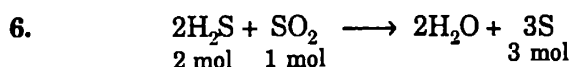
Thus,  $(\text{NH}_4)_3\text{PO}_4$  is the limiting reactant giving 0.1 mol  $\text{Ba}_3(\text{PO}_4)_2$

Thus, (a)

5.  $\text{BaCl}_2$  required by 0.2 mol of  $(\text{NH}_4)_3\text{PO}_4$  = 0.3 mol

$$\text{Thus, } \text{BaCl}_2 \text{ in excess} = 0.5 - 0.3 = 0.2 \text{ mol}$$

Thus, (d)

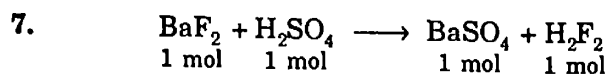


given 1 mol 1 mol ?

Thus,  $\text{H}_2\text{S}$  is the limiting reactant forming 1.5 mol S

Thus, (c)

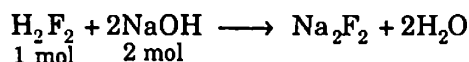
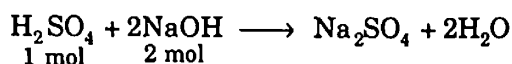




given 1 mol 2 mol

Thus, unreacted  $\text{H}_2\text{SO}_4 = 1 \text{ mol}$

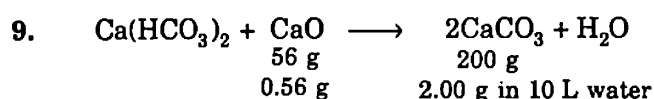
$\text{H}_2\text{F}_2$  formed = 1 mol



Thus, total NaOH required by 1 mol  $\text{H}_2\text{F}_2$  (formed) and 1 mol  $\text{H}_2\text{SO}_4$  (unreacted) = 4 mol

Thus, (a)

8. (b)

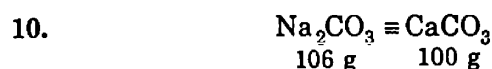


10 L  $\text{H}_2\text{O}$  (=  $10^4 \text{ mL}$ ) has  $\text{CaCO}_3 = 2 \text{ g}$

$10^6 \text{ mL}$  (ppm) has  $\text{CaCO}_3 = 200 \text{ g}$

Thus, 200 ppm  $\text{CaCO}_3$

Thus, (a)



Hardness in  $10^6 \text{ g H}_2\text{O} = 100 \text{ g CaCO}_3$

$\therefore$  Hardness in 10 L ( $10^4 \text{ mL} = 10^4 \text{ g H}_2\text{O}$ ) = 1 g  $\text{CaCO}_3$

100 g  $\text{CaCO}_3$  required = 106 g  $\text{Na}_2\text{CO}_3$

$\therefore$  1 g  $\text{CaCO}_3$  required = 1.06 g  $\text{Na}_2\text{CO}_3$

Thus, (d)

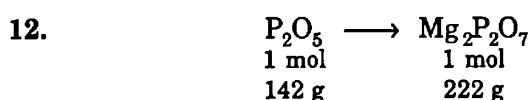
11. Iron oxide = 0.5434 g

Oxygen lost as  $\text{H}_2\text{O} = 0.1210 \text{ g}$

Iron =  $0.5434 - 0.1210 = 0.4224 \text{ g}$

| Element | Amount   | %     | mole | Ratio |
|---------|----------|-------|------|-------|
| Iron    | 0.4224 g | 77.73 | 1.39 | 1     |
| Oxygen  | 0.1210 g | 22.26 | 1.39 | 1     |

Thus, FeO (a)

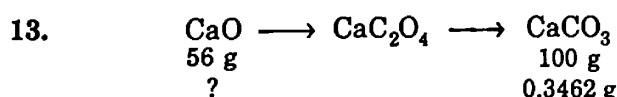


$$\text{P}_2\text{O}_5 \text{ in the mineral} = 0.5428 \times \frac{26.26}{100}$$

$$= 0.1425 \text{ g} = 1 \times 10^{-3} \text{ mol}$$

Thus,  $\text{Mg}_2\text{P}_2\text{O}_7$  obtained =  $1 \times 10^{-3} \text{ mol} = 0.2228 \text{ g}$

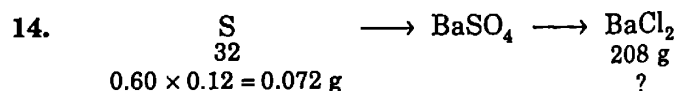
Thus, (d)



$$\text{Pure CaO in the mineral} = \frac{56}{100} \times 0.3462$$

$$\begin{aligned} &= 0.1938 \text{ g} \\ \therefore \quad \% \text{ of pure CaO} &= \frac{0.1938}{0.8432} \times 100 \\ &= 23\% \end{aligned}$$

Thus, (b)



$\text{BaCl}_2$  required by 0.072 g sulphur to be precipitated as

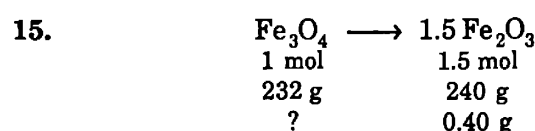
$$\text{BaSO}_4 = \frac{208}{32} \times 0.072$$

$$= 0.468 \text{ g}$$

$$\text{Thus, volume of BaCl}_2 \text{ solution} = \frac{0.468 \times 100}{1.6}$$

$$= 29.25 \text{ mL}$$

Thus, (c)



$$\text{Fe}_3\text{O}_4 \text{ required by } 0.40 \text{ g Fe}_2\text{O}_3 = \frac{232}{240} \times 0.4$$

$$= 0.3867 \text{ g (pure)}$$

$$= 0.3867 \times \frac{100}{18} \text{ g}$$

$$= 2.15 \text{ g impure Fe}_3\text{O}_4$$

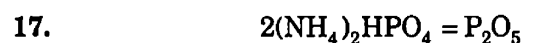
Thus, (a)

16. 10 g glucose is in = 100 mL

$$\therefore 180 \text{ g glucose is in} = \frac{100 \times 180}{10} \text{ mL}$$

$$= 1800 \text{ mL} = 1.8 \text{ L}$$

Thus, (c)



$$2 \times 132 \text{ g} = 142 \text{ g}$$

$$\text{Thus, \% of P}_2\text{O}_5 = \frac{142}{264} \times 100 = 53.78$$

Thus, (d)

18. Oxygen = 67.6%

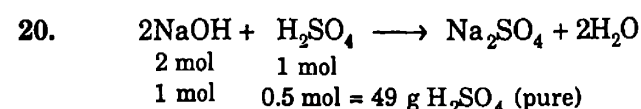
Metal = 32.33%

Thus, 67.67 g oxygen combines with = 32.33 g metal

$$\text{hence, 8 g oxygen combines with} = \frac{32.33 \times 8}{67.67} = 3.82$$

Thus, (b)

19. (a)



$$\text{Thus, } 70\% \text{ H}_2\text{SO}_4 \text{ required} = 49 \times \frac{100}{70} = 70 \text{ g}$$

Thus, (a)

21. (d)

$$22. \text{ Solute present in 800 g solution} = 800 \times \frac{40}{100} \\ = 320 \text{ g}$$

$$\text{Solute precipitated} = 100 \text{ g}$$

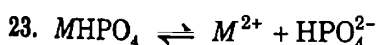
$$\text{Solute left} = 220 \text{ g}$$

$$\therefore \text{ Total weight of solution} = 800 - 100 = 700 \text{ g}$$

$$700 \text{ g solution has solute} = 220$$

$$100 \text{ g solution has solute} = \frac{220}{700} \times 100 \\ = 31.43\%$$

Thus, (a)

Thus, metal is divalent forming  $\text{MCl}_2$ 

Thus, (d)

$$24. \text{ Equivalent weight of } \text{M}^{2+} = 37.2$$

$$\text{Thus, molar mass of } \text{M}^{2+} = 37.2 \times 2 = 74.4$$

$$\text{Thus, molar mass of } \text{MCl}_2 = 74.4 + 71 = 145.5$$

Thus, (c)

$$25. \text{ Glucose in 500 mL solution} = \frac{9 \times 500}{100}$$

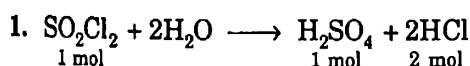
$$= 45 \text{ g}$$

$$= \frac{45}{180} = 0.25 \text{ mol}$$

$$= 0.25 \times 6.02 \times 10^{23} \text{ molecules}$$

$$= 1.5 \times 10^{23}$$

Thus, (c)

**One or More Than One Options Correct**

$$1 \text{ mol H}_2\text{SO}_4 \equiv 1 \text{ mol Ca(OH)}_2 \equiv 2 \text{ mol KOH}$$

$$1 \text{ mol HCl} \equiv \frac{1}{2} \text{ mol Ca(OH)}_2 \equiv 1 \text{ mol KOH}$$

$$2 \text{ mol HCl} \equiv 1 \text{ mol Ca(OH)}_2 \equiv 2 \text{ mol KOH}$$

Thus, mixture of 1 mol  $\text{H}_2\text{SO}_4$  and 2 mol  $\text{HCl}$  requires2 mol  $\text{Ca(OH)}_2$  thus, (a) is correct4 mol  $\text{KOH}$  thus, (d) is correct

$$2. \text{ Iron in haemoglobin} = \frac{4 \times 56}{65000} \times 100 = 0.35$$

Thus, (a) is true

Iron in mole haemoglobin = 224 g

Thus, (b) is false and (c) is true

Molar mass of haemoglobin if iron content is 0.56%

$$= \frac{100 \times 4 \times 56}{0.56} = 40000 < 65000$$

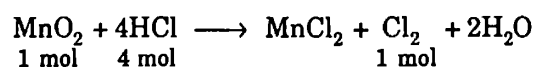
Thus, molar mass is decreased

Thus, (d) is also false

Thus, (a), (c)

3. (a), (c), (d)

$$4. 146 \text{ g HCl} = \frac{146}{36.5} = 4 \text{ mol}$$



|         |         |         |         |
|---------|---------|---------|---------|
| Initial | 0.8 mol | 3.2 mol | 0 mol   |
| after   | 0 mol   | 0.8 mol | 0.8 mol |

Thus,  $\text{MnO}_2$  (less) is limiting reagent thus, (d) is true  
 $\text{HCl}$  (more) is in excess.Amount of product is decided by  $\text{MnO}_2$  $\text{Cl}_2$  formed = 0.8 mol thus (a) is true $\text{HCl}$  unreacted = 0.8 mol thus, (b) is true

Thus, (a), (b), (c) and (d) are correct alternates

$$5. \text{Mg} = 0.273 \text{ g}$$

Product formed with nitrogen = 0.378 g

Nitrogen reacted = 0.105 g

| Element | Amount  | Mole   | Rate | Whole number |
|---------|---------|--------|------|--------------|
| Mg      | 0.273 g | 0.011  | 1.5  | 3            |
| N       | 0.105   | 0.0075 | 1.0  | 2            |

Thus,  $\text{Mg}_3\text{N}_2$ 

Thus, (b)

| Species              | Amount | Mole | Total atoms | H-atoms   |
|----------------------|--------|------|-------------|-----------|
| $\text{CH}_4$        | 1.6 g  | 0.1  | $0.5 N_0$   | $0.4 N_0$ |
| $\text{NH}_3$        | 1.7 g  | 0.1  | $0.4 N_0$   | $0.3 N_0$ |
| $\text{H}_2\text{O}$ | 1.8 g  | 0.1  | $0.3 N_0$   | $0.2 N_0$ |

They have equal number of moles thus, (a) is true  
Number of atoms is  $\text{CH}_4 > \text{NH}_3 > \text{H}_2\text{O}$  thus, (b) is also true

Ratio of H-atom 4 : 3 : 2 thus, (c) is also true.

Thus, (a), (b) and (c)

$$7. \text{H}_2\text{O} = 1 \text{ g mL}^{-1} = 1000 \text{ g L}^{-1}$$

$$= \frac{1000}{18} = 55.55 \text{ mol L}^{-1}$$

Thus, (a) is true

$$1 \text{ g} = \frac{1}{18} \text{ mol} = \frac{6.02 \times 10^{23}}{18} \text{ H}_2\text{O molecules} \\ = 3.33 \times 10^{22} \text{ H}_2\text{O molecules}$$

Thus, (b) is true

It has  $6.06 \times 10^{22}$  H-atoms thus (c) is falseIt has  $3.33 \times 10^{22}$  O-atoms thus (d) is also false

Thus, (a) and (b)

8. 1 mole of  $(\text{NH}_3)_2\text{HPO}_4$  has 0.5 mole  $\text{P}_2\text{O}_5$  and 2 mole of  $\text{NH}_3$ .

Thus, 1 mole (= 132 g)  $(\text{NH}_3)_2\text{HPO}_4$  has = 0.5 mole (= 71 g)  $\text{P}_2\text{O}_5$

$$\% \text{ of } \text{P}_2\text{O}_5 = \frac{71}{132} \times 100 = 53.78\%$$

Thus, (a) is correct.

Also, 132 g  $(\text{NH}_3)_2\text{HPO}_4$  has = 34 g  $\text{NH}_3$

$$\text{Thus, } \% \text{ as } \text{NH}_3 = \frac{34}{132} \times 100 = 25.76\%$$

Thus, (b) is correct.

Also, 132 g has = 28 g N, 9g H and 64 g O

Thus, % of O is maximum

Thus, (c) and (d) are incorrect.

Thus, (a) and (b)

9. Mole fraction of ethanol  $(\text{C}_2\text{H}_5\text{OH}) = 0.25 = \frac{n_1}{n_1 + n_2}$

$$\text{Mole fraction of water } (\text{H}_2\text{O}) = 0.75 = \frac{n_2}{n_1 + n_2}$$

$$\therefore \frac{n_1}{n_2} = \frac{0.25}{0.75} = \frac{1}{3}$$

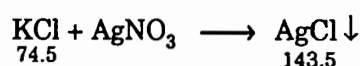
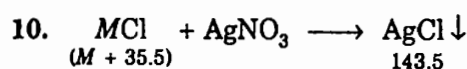
$$\text{C}_2\text{H}_5\text{OH} = n_1 = 1 \text{ mole} = 46 \text{ g}$$

$$\text{H}_2\text{O} = n_2 = 3 \text{ moles} = 54 \text{ g}$$

$$\text{Total mass} = 46 + 54 = 100 \text{ g}$$

Thus, it is 46% by weight of solution and 54% by weight of solution.

Thus, (c) and (d) are correct.



Let  $\text{MCl} = x \text{ g}$

than  $\text{KCl} = (12.8 - x) \text{ g}$

$$\text{AgCl due to MCl} = \frac{143.5x}{(M + 35.5)}$$

$$\text{AgCl due to KCl} = \frac{143.5}{74.5} (12.8 - x)$$

$$\frac{143.5x}{(M + 35.5)} + \frac{143.5(12.8 - x)}{74.5} = 28.7$$

Since, MCl is volatile, in second case AgCl due to MCl only.

$$\text{Thus, } \left( \frac{143.5x}{M + 35.5} \right) = 14.35$$

$$\therefore 14.35 + \frac{143.5(12.8 - x)}{74.5} = 28.7$$

$$1 + \frac{10(12.8 - x)}{74.5} = 2$$

$$(12.8 - x) = 7.45$$

$$x = 5.35 \text{ g}$$

$$\text{Thus, } \frac{143.5 \times 5.35}{(M + 35.5)} = 14.35$$

$$\therefore M = 18$$

Thus, ionic mass of  $M^+ = 18$ , thus (a) is true and molar mass of  $\text{MCl} = 53.5$

$$\text{Thus, moles of MCl} = \frac{5.35}{53.5} = 0.1$$

$$\text{Moles of KCl} = \left( \frac{12.80 - 5.35}{74.5} \right) = 0.1$$

Thus, (b) is also true

Thus, (c) is also true

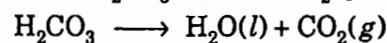
$\text{AgCl}$  is water insoluble

Thus, (d) is false

Thus, (a), (b) and (c)

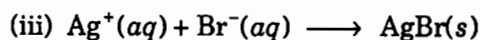
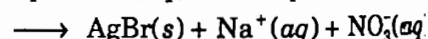
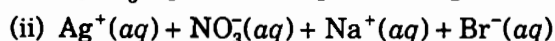
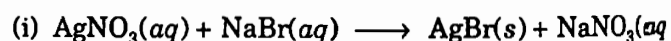
## Brain Twisters

1. Heat evolved in the reaction (exothermic) causes decomposition of  $\text{H}_2\text{CO}_3(aq)$  into  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(l)$

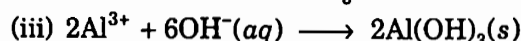
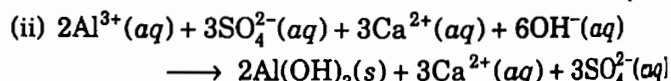
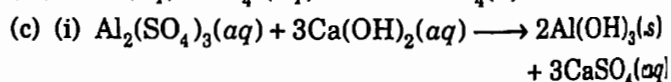
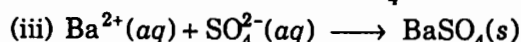
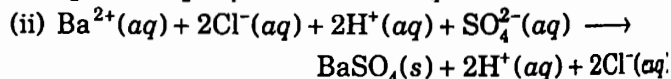
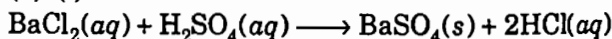


Thus,  $\text{H}_2\text{CO}_3$  is unstable.

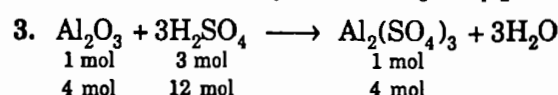
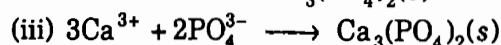
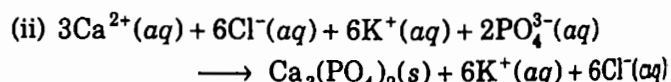
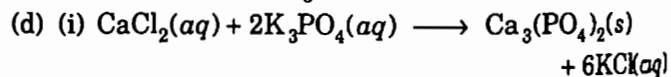
2. (a)



(b) (i)

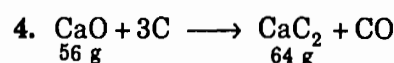


$\text{NaOH}$  dissolves  $\text{Al}(\text{OH})_3$  hence can't be used



$\text{H}_2\text{SO}_4$  required = 12 mol

$\text{Al}_2(\text{SO}_4)_3$  formed = 4 mol



Crude produce is = 85%  $\text{CaC}_2$  + 15%  $\text{CaO}$  (unreacted)

$$450 \text{ kg of crude product has } 15\% \text{ CaO} = 450 \times \frac{15}{100} \\ = 67.50 \text{ kg CaO}$$

$$\text{and } 85\% \text{ CaC}_2 = 450 \times \frac{85}{100} \\ = 382.5 \text{ kg CaC}_2$$

$$64 \text{ kg CaC}_2 \text{ is from } = 56 \text{ g CaO}$$

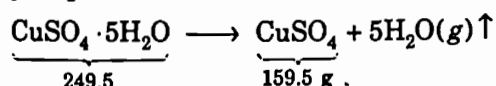
$$\text{Thus, } 382.5 \text{ kg CaC}_2 \text{ is from } = \frac{56}{64} \times 382.5 \\ = 334.69 \text{ kg CaO}$$

$$\text{Thus, total CaO required} = 67.50 + 334.69 \\ = 402.19 \text{ kg}$$

$$(b) 382.5 \text{ kg CaC}_2$$

$$5. \text{CuSO}_4 = x \text{ g}$$

$$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = (1.245 - x)$$



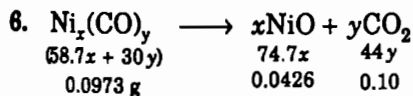
$$\text{CuSO}_4 \text{ in } (1.245 - x) \text{ g}$$

$$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = \frac{159.5}{249.5} (1.245 - x) \text{ g}$$

$$\text{Thus, } \frac{159.5}{249.5} (1.245 - x) + x = 0.832$$

$$x = 0.1 \text{ g}$$

$$\therefore \text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 1.145 \text{ g}$$



$$\begin{array}{ccc} 58.7x + 30y & 74.7x & 44y \\ 0.0973 \text{ g} & 0.0426 & 0.10 \end{array}$$

$$\frac{74.7x}{44y} = \frac{0.0426}{0.10}$$

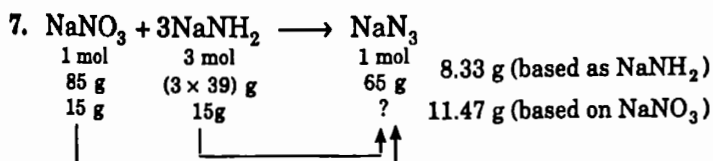
$$\therefore \frac{x}{y} = 0.25 = \frac{1}{4}$$

$$\text{Thus, empirical formula is } = \text{Ni}(\text{CO})_4$$

$$7. 3 \text{ mol NaNH}_2 \text{ form } = 1 \text{ mol NaN}_3$$

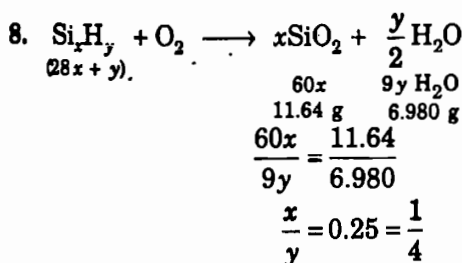
$$0.0769 \text{ mol NaNH}_2 \text{ forms } = 0.0256 \text{ NaN}_3$$

$$\text{Thus, NaNH}_2 \text{ is limiting reactant and NaN}_3 \text{ obtained} \\ = 0.0256 \text{ mol}$$

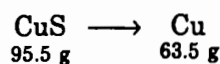
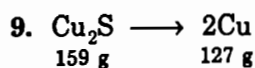


$$\text{Limiting reagent is NaNH}_2$$

$$\text{and thus NaN}_3 \text{ obtained is } 8.33 \text{ g}$$



$$\text{Thus, Si}_x\text{H}_y \text{ is SiH}_4$$



There is 11.0% impurity. Thus, mixture has 89.0 g of Cu<sub>2</sub>S and CuS.

$$\text{Let Cu}_2\text{S} = x \text{ g}$$

$$\text{then CuS} = (89.0 - x) \text{ g}$$

$$\text{Thus, Cu obtained from } x \text{ g Cu}_2\text{S} = \left( \frac{127x}{159} \right) \text{ g}$$

$$\text{and from } (89.0 - x) \text{ g CuS} = \frac{63.5(89.0 - x)}{95.5} \text{ g}$$

$$\text{Total Cu obtained}$$

$$\frac{127x}{159} + \frac{63.5(89.0 - x)}{95.5} = \frac{75.4 \times 89.5}{100} \text{ (given)} \\ = 67.483 \text{ g}$$

$$\text{This gives } x = \text{Cu}_2\text{S} = 62.45$$

$$\% \text{ of Cu}_2\text{S} = 62.45\%$$

$$\text{CuS} = 27.55\%$$

$$10. 0.033 \text{ mol C}_2\text{H}_5\text{OH per litre} = 0.033 \times 46 \times 1000 \text{ mg/L}$$

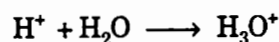
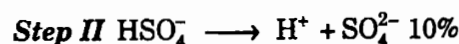
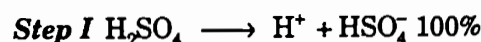
$$= 1518 \text{ mg/L}$$

$$= 151.8 \text{ mg/dL}$$

This excess prescribed limit, hence **yes DWI ticket**

## Passage Comprehension Questions

### Passage 1



SO<sub>4</sub><sup>2-</sup> is from step II

$$\text{Step I is 100\% thus } [\text{H}^+] = 0.2 \text{ M}$$

$$\text{and } [\text{HSO}_4^-] = 0.2 \text{ M}$$

$$\text{Step II is 10\% thus } [\text{H}^+] = 0.2 \times 0.1 = 0.02 \text{ M}$$

$$\text{and } [\text{SO}_4^{2-}] = 0.02 \text{ M}$$

$$\text{total } [\text{H}_3\text{O}^+] = 0.2 + 0.02 = 0.22 \text{ M}$$

$$[\text{SO}_4^{2-}] = 0.02 \text{ M}$$

$$\text{and } [\text{HSO}_4^-] = 0.20 - 0.02 = 0.18 \text{ M}$$

$$1. (d) \quad 2. (c) \quad 3. (b) \quad 4. (b)$$

### Passage 2

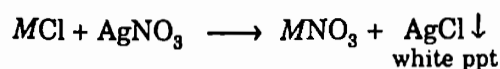
$$1. (a) \quad 2. (a,b)$$

### Passage 3

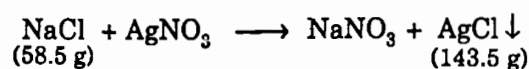
$$1. (a) \quad 2. (b) \quad 3. (a)$$

## Passage 4

1. Let
- $MCl = x$
- g,
- $NaCl = (11.2 - x)$
- g

 $(M + 35.5)$  g  $MCl$  gives = 143.5 g  $AgCl$ 

$$x \text{ g } MCl \text{ gives } = \frac{143.5x}{(M + 35.5)} \text{ g } AgCl \quad \dots(i)$$



$$(11.2 - x) \text{ g } NaCl \text{ gives } = \frac{143.5(11.2 - x)}{58.5} \text{ g } AgCl \quad \dots(ii)$$

$$\frac{143.5x}{M + 35.5} + \frac{143.5(11.2 - x)}{58.5} = 28.7 \text{ (given)} \quad \dots(iii)$$

On heating  $MCl$  vaporises (being volatile)Thus,  $AgCl$  is due to  $MCl$  only

$$\text{Thus, } \frac{143.5x}{M + 35.5} = 14.35 \quad \dots(iv)$$

Thus, from (III)

$$\frac{143.5(11.2 - x)}{58.5} = 14.35$$

Thus, gives  $x = 5.35$ From (IV)  $M = 18$ 

MCl in mixture = 5.35 g

NaCl in mixture = 5.85 g

Thus, ionic mass of  $M^+$  is 18.Also, molar mass of  $MCl = 53.5 \text{ g mol}^{-1}$ 

$$\text{moles of } MCl = \frac{5.35}{53.5} = 0.1$$

$$\text{moles of } NaCl = \frac{5.85}{58.5} = 0.1$$

Total moles = 0.2

Mole fraction of  $MCl = 0.5$ Mole fraction of  $MCl = 0.5$ 

Thus, 1. (a) 2. (b) 3. (a)

## Passage 5

$$1. (a) \quad 10 \text{ g } K_2PtCl_6 = \frac{10}{417} \text{ mol} = 0.024 \text{ mol (limiting)}$$

$$10 \text{ g } NH_3 = \frac{10}{17} = 0.588 \text{ mol (excess)}$$

 $K_2PtCl_6$  consumed = 0.024 mol = *cis*-platin formed $NH_3$  consumed = 0.048 mol $NH_3$  unreacted = 0.588 - 0.048

= 0.54 mol

2. (b) 3. (a) 4. (b) 5. (c)

## Passage 6

$$1. (b) \quad 310 \text{ g } P_4 = \frac{310}{124} \text{ mol } P_4 = 10 \text{ mol } H_3PO_4$$

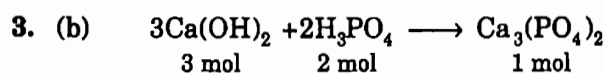
$$2. (c) \quad 2.5 \text{ mol } P_4O_{10} \text{ (100\% yield)}$$

$$= 2.5 \times \frac{50}{100} \quad (50\% \text{ yield})$$

$$= 2.5 \times 0.5 \times 0.25 \times 4$$

(25% yield)

$$= 1.25 \text{ mol } H_3PO_4$$



$$1 \text{ mol } Ca(OH)_2 = \frac{1}{3} \text{ mol } Ca_3(PO_4)_2$$

$$2 \text{ mol } H_3PO_4 = 1 \text{ mol } Ca_3(PO_4)_2$$

$$1.25 \text{ mol } H_3PO_4 = \frac{1.25}{2} \text{ mol.}$$

 $Ca(OH)_2$  is limiting reagent.

## Passage 7

$$1. (c) \quad 5.8 \text{ g } NaIO_3 = \frac{5.8}{198} \text{ mol } NaIO_3$$

$$\therefore NaHSO_3 = 3 \times \frac{5.8}{198} \text{ mol}$$

$$= \frac{3 \times 5.8}{198} \times 104 \text{ g } NaHSO_3$$

$$= 9.14 \text{ g}$$

$$2. (a) \quad I^- \text{ formed in step I} = \frac{5.8}{198} \text{ mol}$$

$$IO_3^- \text{ required in step II} = \frac{5.9}{198 \times 5} \text{ mol}$$

$$= \frac{5.8 \times 198}{198 \times 5} \text{ g } NaIO_3$$

$$= 1.16 \text{ g } NaIO_3$$

$$\therefore \text{Volume} = \frac{1.16}{5.8} = 0.2 \text{ L}$$



Change in oxidation number = 6 units

Thus, one mole  $NaIO_3 = 6$  equivalents

$$4. (d) \quad 1.16 \text{ g } NaIO_3 = \frac{1.16}{198} \text{ mol}$$

$$= \frac{6.96}{198} \text{ equivalent (since } IO_3^- = 6)$$

$$= 0.035 \text{ equivalent}$$

## Passage 8

$$1. (a) \quad 0.74 \text{ g } O_3 = \frac{0.74}{48} = 0.0154 \text{ mol } O_3$$

$$0.67 \text{ g } NO = \frac{0.67}{30} = 0.0223 \text{ mol } NO$$

 $O_3$  is the limiting reagent and  $NO$  is in excess

$$= 0.0223 - 0.0154 = 0.007 \text{ mol}$$

Thus,  $O_3$  taken =  $NO_2$  formed

$$= 0.0154 \text{ mol } NO_2$$

$$= 0.0154 \times 46 \text{ g } NO_2$$

$$= 0.71 \text{ g}$$

2. (b) 3. (c)

## Passage 9

1. (c) 2. (d) 3. (a)

## Assertion &amp; Reason

1. (d) 2. (a) 3. (d) 4. (a) 5. (b)

## True &amp; False

1. F 2. T 3. F 4. F 5. F 6. T 7. F
- 
8. T 9. T 10. T

## Fill in the Blanks

1. 1.12 2. 17.75 3. 4 4.
- $\text{H}_2\text{S}$
- 5.
- $\text{HCl}$

## Matrix-Match Type Questions

## I. Only One Correct

1. (A) — (4); (B) — (5); (C) — (2);
- 
- (D) — (1); (E) — (3)
- 
2. (A) — (3); (B) — (4); (C) — (1); (D) — (2);

## II. One or More Correct

1. (A) — (1,2,3); (B) — (1,3); (C) — (1,4,5);
- 
- (D) — (1,4,5); (E) — (1,4,5)

## Integer Answer Types

## Set I

|             |   |   |   |   |   |   |   |   |
|-------------|---|---|---|---|---|---|---|---|
| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Answers →   | 4 | 5 | 2 | 1 | 4 | 6 | 2 | 1 |
|             | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
|             | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|             | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
|             | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
|             | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
|             | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
|             | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
|             | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
|             | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
|             | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |

## Set II

|             |   |   |   |   |   |   |   |   |
|-------------|---|---|---|---|---|---|---|---|
| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Answers →   | 3 | 2 | 4 | 7 | 5 | 2 | 1 | 2 |
|             | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
|             | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|             | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
|             | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
|             | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
|             | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
|             | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
|             | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
|             | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
|             | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |



Phenolphthalein is colourless in acidic solution and pink in alkaline solution. Methyl-red is red in acidic solution and yellow in alkaline solution. What is an idea? A drop of phenolphthalein or methyl red can indicate completion of acid-alkali reaction by colour change in volumetric titration.

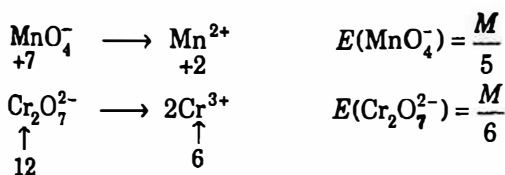
# Volumetric

## Quick Points

- Mole =  $\frac{\text{mass}}{\text{molar mass}}$
- $N_0$  (Avogadro's number) =  $6.02 \times 10^{23} \text{ mol}^{-1}$   
1 equivalent of an acid  $\equiv$  1 equivalent of a base in an acid-base reaction  
1 equivalent of a reducing agent  $\equiv$  1 equivalent of an oxidising agent in a redox reaction

Equivalent weight in a redox reaction

$$= \frac{\text{molar mass (one unit)}}{\text{change in O.N. (equal on both sides)}}$$



$$\Delta G^\circ = -nFE^\circ$$

For redox reactions such that  $\Delta G_1^\circ + \Delta G_2^\circ = \Delta G_3^\circ$

$$E_3^\circ = \frac{n_1 E_1^\circ + n_2 E_2^\circ}{n_3}$$

where  $n_i$  is the number of electrons exchanged in a reaction with standard electrode potential  $E_i^\circ$ ,  $F$  is number of coulombs (1 F = 96500 coulombs)

Electrode potential is given by Nernst equation

$$E = E^\circ - \frac{2.303RT}{nF} \log Q$$

## Learning Framework of the Chapter

- Titrimetry
- Methods of Expressing Concentration of a Solution
- Mole Fraction
- Per cent Concentration
- Molarity ( $M$ )
- Molality ( $m$ )
- Equivalent Mass and Normality
- Volumetric Titrations
- Acid-Base Titrations
- Redox Titrations
- Iodometric/Iodimetric Titrations



where,  $Q$  is reaction quotient.

At equilibrium,  $E = 0$  and  $Q = K_{eq}$

$$\therefore E^\circ = \frac{2.303RT}{nF} \log K_{eq}$$

$$E^\circ = \frac{0.0591}{n} \log K_{eq}$$

$$\text{(at 298 K when } \frac{2.303RT}{F} = 0.0591 \text{ V)}$$

## Titrimetry

Titrimetric methods include a large and powerful group of quantitative methods that are based on measuring the amount of a reagent of known concentration that is consumed in an analysis. Titrimetric can be

| Volumetric                                                                                                                      | Gravimetric                                                 | Coulometric                                                                                    |
|---------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| involves measuring the volume of a solution of known concentration that is needed to react with the species under investigation | involves measurement of mass involved instead of its volume | involves measurement of electric current required to bring about a particular chemical change. |

Present unit describes stoichiometric based on **Volumetric Titrimetry**.

### Terms to be used in Volumetric Titrimetry

A **standard solution** (or a **standard titrant**) is a reagent of known concentration that is used to carry out a titrimetric analysis.

A **titration** is performed by slowly adding a standard solution from a burette to a solution under examination (analyte) until the reaction between the two is judged complete. The volume or mass of reagent needed to complete the titration is determined from the difference between the initial and final readings.

It is sometimes necessary to add an excess of the standard titrant and then determine the excess amount by **back-titration** with a second standard titrant.

### Primary and Secondary Standards

A **primary standard** is a highly purified compound that serves as a reference material in volumetric and mass titrimetric methods. The accuracy of a method is mainly dependent on the properties of this compound. A primary standard must be

1. of high purity
2. of atmospheric stability, (no oxidation, reduction or decomposition)
3. anhydrous so that composition of the solid does not change with variation in humidity
4. of reasonable solubility in the titration medium
5. of reasonably large molar mass so that the relative error associated with weighing the standard is minimised.

In most of the cases, above requirements are not met and their standard solutions cannot be prepared by dissolving a weighed amount in a given volume of solution. They are termed as **secondary standard**.

### Standard Solutions

The ideal standard solution (of known concentration) must

- be sufficiently stable so that it is necessary to determine its concentration only once.
- react rapidly with the analyte.
- give sharp end-point with the analyte.
- If concentration can be known simply by dissolving the known amount in a given volume of solutions, they are termed as **primary standard solutions**. In most cases, concentration can be determined by standardisation against primary standard solution. Such solutions are termed as **secondary standard solution**.

### Equivalence Points and End Points

The equivalent point in a titration is a theoretical point reached when the amount of added titrant is chemically equivalent to the amount of analyte in the sample. Equivalent point cannot be determined experimentally. We can only estimate its position by observing same physical change associated with the condition of equivalence. This is called end-point of titration.

Equivalent point is reached when 1 mole of HCl is neutralised by 1 mole of NaOH. But we cannot detect this equivalent point. If one drop of suitable indicator (in this case phenolphthalein) is added in the HCl (analyte) then additional drop of NaOH (from burette) will give light pink colour. This is the end-point. Thus volume of titrant at the end-point is larger than that at the equivalent point.

Sometimes even rough estimate of the concentration is not known. In such cases excess of reagent is added so that complete reaction of the analyte takes place. Suppose we have been given  $\text{NH}_3$  solution. We allow its reaction with excess of HCl or  $\text{H}_2\text{SO}_4$  of known concentration. Acid reacts equivalent to  $\text{NH}_3$  and unreacted acid is determined by titration with NaOH. Estimation of unreacted acid by NaOH is called **back titration**.

### Explanation of Terms

We can determine the concentration of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ), potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) by dissolving the known amount in a given volume of solution. These are stable to atmospheric condition and their concentration does not change. They are thus, **primary standard**. Ferrous salts ( $\text{Fe}^{2+}$  as  $\text{FeSO}_4$ ), potassium permanganate ( $\text{KMnO}_4$ ), mineral acids ( $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ), sodium hydroxide ( $\text{NaOH}$ ) etc, are not stable to atmospheric condition. Their

solutions are prepared by dissolving a known amount or volume but they have to be standardised using primary standard. Thus, all these are secondary standard.

| Secondary standard                                                                         | Standardised against primary standard                                                                                       |
|--------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------|
| NaOH                                                                                       | H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (oxalic acid)                                                                  |
| KMnO <sub>4</sub>                                                                          | H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>                                                                                |
| FeSO <sub>4</sub> · 7H <sub>2</sub> O                                                      | K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>                                                                               |
| Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> · 5H <sub>2</sub> O<br>(sodium thiosulphate) | CuSO <sub>4</sub> · 5H <sub>2</sub> O                                                                                       |
| HCl, HNO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub>                                     | NaOH (standardised with H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> )                                                      |
| I <sub>2</sub>                                                                             | Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> · 5H <sub>2</sub> O (standardised with CuSO <sub>4</sub> · 5H <sub>2</sub> O) |

**Mineral acids** are standardised using sodium hydroxide which is in turn standardised first using oxalic acid.

Iodine is standardised using sodium thiosulphate which in turn is standardised first using copper sulphate solution.

## Methods of Expressing Concentration of a Solution

The concentration of a chemical **solution** refers to the amount of **solute** that is dissolved in a **solvent**. We normally think of a solute as a solid that is added to a solvent (for example NaCl in H<sub>2</sub>O) but the solute could exist in another phase. For example, if we add a small amount of ethanol (C<sub>2</sub>H<sub>5</sub>OH) to water, then the ethanol is solute and the water is the solvent. If we add a smaller amount of water to a larger amount of ethanol, then water could be solute.

The amount of solute in a solution can be expressed in terms of two system of units:

- 'Group A' units specify the amount of solute in a given volume of solution, such as density, molarity, etc.
- 'Group B' units specify the amount of solute for a given mass of solvent or solution, such as mass%, mole fraction, molality, etc.

**The advantage of 'group A' units is the ease of solution preparation and that of 'group B' units is temperature independence.**

In a given solution, let solute be represented by (1) and the solvent by (2)

$$w_1 = \text{mass of solute}$$

$$w_2 = \text{mass of solvent}$$

$$m_1 = \text{molar mass of solute}$$

$$m_2 = \text{molar mass of solvent}$$

$$n_1 = \text{moles of solute} = \frac{w_1}{m_1}$$

$$n_2 = \text{moles of solvent} = \frac{w_2}{m_2}$$

$$w_1 + w_2 = \text{mass of solution}$$

$$(n_1 + n_2) = \text{moles of solution}$$

$$d = \text{density in g cm}^{-3}$$

$$V = \text{volume of solution in cm}^3$$

$$E_1 = \text{equivalent weight of solute}$$

## Expressing Concentration in Groups A and B

Following are the terms given in Tables 7.1 and 7.2 widely used to express concentration of solution.

Table 7.1 Expressing Concentration in "Group A"

| Name             | Symbol | Definition                                                                                              | Formula                    | Usual SI unit            |
|------------------|--------|---------------------------------------------------------------------------------------------------------|----------------------------|--------------------------|
| Volume per cent  | C      | amount of solute present in 100 mL of solution                                                          | $C = \frac{100w_1}{V}$     | kg m <sup>-3</sup>       |
| Volume per litre | C      | amount of solute present in 1000 mL of solution                                                         | $C = \frac{1000w_1}{V}$    | g L <sup>-1</sup>        |
| Molarity         | M      | number of moles of solute present in 1 L (1 dm <sup>3</sup> , 1000 cm <sup>3</sup> ) of solution        | $M = \frac{1000w_1}{m_1V}$ | mol dm <sup>-3</sup>     |
| Normality        | N      | number of g-equivalent of solute present in 1 L (1 dm <sup>3</sup> , 1000 cm <sup>3</sup> ) of solution | $N = \frac{1000w_1}{E_1V}$ | g equiv dm <sup>-3</sup> |

Table 7.2 Expressing Concentrations in "Group B"

| Name                                | Symbol | Definition                                                     | Formula                                                                           | Usual SI unit        |
|-------------------------------------|--------|----------------------------------------------------------------|-----------------------------------------------------------------------------------|----------------------|
| % concentration by mass of solution | %      | amount of solute present in 100 g of solution.                 | $\% = \frac{100w_1}{w_1 + w_2}$                                                   | dimensionless        |
| % concentration by mass of solvent  | %      | amount of solute present in 100 g of solvent                   | $\% = \frac{100w_1}{w_2}$                                                         | dimensionless        |
| Molality                            | m      | number of moles of solute present in 1 kg solvent              | $m = \frac{1000w_1}{m_1w_2}$                                                      | mol kg <sup>-1</sup> |
| Mole fraction                       | X      | fraction of a component out of total moles present in solution | $X_1 = \frac{n_1}{n_1 + n_2}$<br>$X_2 = \frac{n_2}{n_1 + n_2}$<br>$X_1 + X_2 = 1$ | dimensionless        |

Standard notation for molality is *m* and should not be confused with *m*<sub>1</sub> (molar mass of solute) or *m*<sub>2</sub> (molar mass of solvent)

Closely related to weight per cent and particularly useful for dilute solutions are the concentration units parts per million (ppm) and parts per billion (ppb)

$$\text{Parts per million (ppm)} = \frac{\text{mass of solute component}}{\text{total mass of solution}} \times 10^6$$

$$\text{Parts per billion (ppb)} = \frac{\text{mass of solute component}}{\text{total mass of solution}} \times 10^9$$

## Mole Fraction

Fraction of the substance in the mixture expressed in terms of mole is called its mole fraction.

$$n_A = \text{moles of A in mixture of A and B}$$

$$n_B = \text{moles of B in same mixture}$$

$$\text{mole fraction of A in the mixture} = X_A = \frac{n_A}{n_A + n_B}$$

$$\text{mole fraction of B in the mixture} = X_B = \frac{n_B}{n_A + n_B}$$

This is thus, the number of moles of a compound divided by the total number of moles of all chemical species in the solution. Keep in mind, the sum of all mole fractions in a solution always equals 1.

$$\begin{aligned} \text{Thus,} \quad X_A + X_B &= 1 \\ X_A &= 1 - X_B \end{aligned}$$

**Illustration 1** What are the mole fractions of the components of the solution formed when 92 g glycerol ( $92 \text{ g mol}^{-1}$ ) is mixed with 90 g water ( $18 \text{ g mol}^{-1}$ )?

### Solution

| Components | Step 1                                                                                                        | Step 2                          | Step 3                                                                                                         |
|------------|---------------------------------------------------------------------------------------------------------------|---------------------------------|----------------------------------------------------------------------------------------------------------------|
| Glycerol   | convert amount into moles<br>$= \frac{\text{amount}}{\text{molar mass}}$<br>$= \frac{92}{92} = 1 \text{ mol}$ | Take total moles = 1 + 5<br>= 6 | Mole fraction = $\frac{\text{mole of the species}}{\text{total moles}}$<br>$X_{\text{glycerol}} = \frac{1}{6}$ |
| Water      | mole = $\frac{90}{18}$<br>= 5 mol                                                                             |                                 | $X_{\text{water}} = \frac{5}{6}$                                                                               |

**Check:** Sum of mole fraction is always equal to one

$$X_{\text{glycerol}} + X_{\text{water}} = \frac{1}{6} + \frac{5}{6} = 1$$

## Per cent Concentration

In a solution, let there be  $w_1 \text{ g}$  solute (molar mass =  $m_1$ )

$w_2 \text{ g}$  solvent (molar mass =  $m_2$ )

$V \text{ mL}$  of solution of density  $d \text{ g/mL}$

There are following types of expressions used to denote % concentration:

(a) mass per cent

$$\begin{aligned} \left( \frac{w}{W} \right) &= \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% \\ &= \left( \frac{w_1}{w_1 + w_2} \times 100 \right) \end{aligned}$$

(b) volume per cent

$$\begin{aligned} \left( \frac{v}{V} \right) &= \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\% \\ &= \frac{v}{V} \times 100 \end{aligned}$$

(c) mass/volume per cent

$$\begin{aligned} \left( \frac{w}{V} \right) &= \frac{\text{mass of solute, g}}{\text{volume of solution, mL}} \times 100\% \\ &= \frac{w}{V} \times 100 \end{aligned}$$

- Note that the denominator in each of these expressions refers to the solution rather than to the solvent.
- (a) and (b) do not depend on the unit employed while (c) has unit of mass/volume (say g/mL).
- Of the three expressions, only mass per cent is **temperature independent**.
- To avoid confusion, we generally use terms like % by **mass of solution** which means amount of solute ( $w_1$ ) g present in 100 g solution

$$= \frac{w_1}{w_1 + w_2} \times 100$$

and % by **mass of solvent** which means amount of solute ( $w_1$ ) g present in 100 g solvent

$$= \frac{w_1}{w_2} \times 100$$

- For every dilute solutions, parts per million,  $10^6$  (ppm) is a convenient way to express concentration.

$$\text{Concentration (ppm)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$$

- For even more dilute solutions, parts per billion,  $10^9$  (ppb) rather than  $10^6$  (ppm) is used.

$$\text{Concentration (ppb)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9$$

- Concentration in parts per thousand (ppt) is also commonly used.

$$\text{Concentration (ppt)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^3$$

**Illustration 1** Aqueous urea solution is 20% by mass of solution. Calculate percentage by mass of solvent.

**Solution** If solute  $w_1 = 20 \text{ g}$

then solution  $w_1 + w_2 = 100 \text{ g}$

$\therefore$  solvent =  $100 - 20 = 80 \text{ g}$

Hence, percentage by mass of solvent =  $\frac{20}{80} \times 100 = 25\%$

**Alternate method** Given,  $\frac{w_1}{w_1 + w_2} \times 100 = 20$

$$\frac{w_1}{w_1 + w_2} = \frac{1}{5}$$

Thus,  $w_1 : (w_1 + w_2) = 1 : 5$

or  $w_1 : w_2 = 1 : 4$

$\therefore \frac{w_1}{w_2} \times 100 = 25\%$

Volume = 100 mL

$$= \frac{100}{1000} \text{ L}$$

$$= 0.1 \text{ L}$$

$$\text{Molarity} = \frac{0.1 \text{ mol}}{0.1 \text{ L}}$$

$$= 1 \text{ mol L}^{-1}$$

**Illustration 2** Equal moles of water and urea are taken in a flask. What is mass percentage of urea in the solution?

**Solution** If  $\text{H}_2\text{O} = x \text{ mol} = 18x \text{ g}$

then urea =  $x \text{ mol} = 60x \text{ g}$

total mass of the solution =  $18x + 60x = 78x \text{ g}$

$$\text{mass percentage of urea} = \frac{18x}{78x} \times 100 = 23.077\%$$

## Molarity (M)

Number of moles of solute present per litre of the solution is its molarity.

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{litres of solution}}$$

If 0.1 mol of a solute is present in 100 mL (0.1 L) solution then molarity

$$M = \frac{0.1}{0.1} = 1 \text{ M}$$

## DEEP Focus

moles of solute = molarity  $\times$  litres of solution

millimoles of solute = molarity  $\times$  mL of solution

## Analytical Molarity

The analytical molarity of a solution gives the total number of moles of a solute in one litre of the solution (or the total number of millimoles in one millilitre). Thus, analytical molarity specifies the amount by which the solution can be prepared.

- Sulphuric acid solution that has analytical concentration of 1 mol per litre can be prepared by dissolving 1.0 mol or 98 g of  $\text{H}_2\text{SO}_4$  in one litre of solution.
- Sodium hydroxide solution that has analytical molarity of 0.1 M has 0.1 mol or 4 g of it in one litre of solution.

**Illustration 1** What is the molarity of solution made when 6 g urea (molar mass  $60 \text{ g mol}^{-1}$ ) is dissolved in water to make 100 mL of solution?

**Solution** Solute =  $6 \text{ g} = \frac{6}{60} = 0.1 \text{ mol}$

## Equilibrium Molarity

The equilibrium molarity expresses the molar concentration of a particular species in a solution at equilibrium. In order to specify the equilibrium molarity of a particular species, it is necessary to know how the solute behaves when it is dissolved in a solvent.

- If **analytical molarity** of NaOH is 0.1 M, then equilibrium molarity of NaOH,  $[\text{NaOH}] = 0.0 \text{ M}$  (assuming 100% ionisation).

that of  $\text{OH}^-$ ,  $[\text{OH}^-] = 0.1 \text{ M}$

and that of  $\text{Na}^+$ ,  $[\text{Na}^+] = 0.1 \text{ M}$



- If  $\text{H}_2\text{SO}_4$  ionises as  $\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$

then 1.0 M  $\text{H}_2\text{SO}_4$  (analytical) has equilibrium concentration as (assume 100% ionisation)

$$[\text{H}_2\text{SO}_4] = 0.0 \text{ M}$$

$$[\text{HSO}_4^-] = 1.0 \text{ M}$$

$$\text{H}^+ \text{ as } [\text{H}_3\text{O}^+] = 1.0 \text{ M}$$

- However, there is no difference between analytical and equilibrium molarity when solute dissolved is non-electrolyte or no ionisation takes place in solution. 1 M glucose (non-electrolyte), 1 M urea (non-electrolyte), etc., are also 1 M as equilibrium molarity.

**Illustration 2** Concentration of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) in normal blood is approximately 90 mg per 100 mL. What is the molarity of the glucose solution in blood?

**Solution** Amount of glucose =  $90 \text{ mg} = \frac{90}{1000} = 0.09 \text{ g}$   
 $= \frac{0.09}{180} = 0.0005 \text{ mol}$

Volume of solution = 100 mL = 0.10 L

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{litres of solution}} = \frac{0.0005}{0.10}$$

$$= 0.005 \text{ M}$$

**Illustration 3** Hydrochloric acid is sold commercially as a 12.0 M solution. How many moles and how many grams of HCl are in 300.0 mL of 12.0 M solution?

**Solution** Molarity =  $\frac{\text{moles of solute}}{\text{litres of solution}}$

$$12.0 = \frac{\text{moles of solute (HCl)}}{0.30 \text{ L}}$$

$$\begin{aligned}
 \text{moles of HCl} &= 12 \times 0.30 \\
 &= 3.6 \text{ mol HCl} \\
 &= 3.6 \times 36.5 \text{ g HCl} \\
 &= 131.4 \text{ g HCl}
 \end{aligned}$$

**Illustration 4** How many moles of solute are present in each of the following solutions?

- (a) 35.0 mL of 0.2 M  $\text{HNO}_3$   
 (b) 175 mL of 0.5 M glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ )

**Solution** Molarity  $\times$  volume in mL = millimoles of solute

- (a)  $35.0 \text{ mL} \times 0.2 \text{ M} = 7.0 \text{ millimol} = 0.007 \text{ mol}$   
 (b)  $175 \text{ mL} \times 0.5 \text{ M} = 87.5 \text{ millimol} = 0.0875 \text{ mol}$

**Illustration 5** How many millilitres of 0.45 M  $\text{BaCl}_2$  solution contain 15.0 g of  $\text{BaCl}_2$  ( $208 \text{ g mol}^{-1}$ )?

**Solution** Let volume of the solution containing 15.0 g  $\text{BaCl}_2$  be  $V$  mL

$$\begin{aligned}
 \therefore V \times 0.45 &= 0.45 V \text{ millimol} = 0.45 V \times 10^{-3} \text{ mol} \\
 \therefore 0.45 V \times 10^{-3} &= \frac{15}{208} \\
 \therefore V &= \frac{15}{208} \times \frac{1000}{0.45} = 160.3 \text{ mL}
 \end{aligned}$$

**Illustration 6** Calculate the molar concentration of a solution that is 50% in  $\text{NaOH}$  (w/W) and has a specific gravity of 1.52.

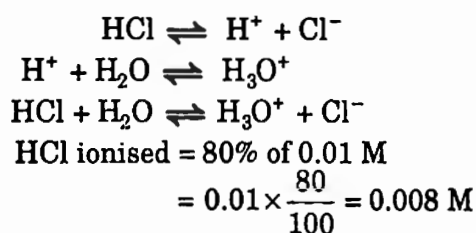
**Solution** Specific gravity =  $\frac{\text{mass}}{\text{volume}} = 1.52$   
 (w.r.t.  $\text{H}_2\text{O} = 1$ )

50%  $\text{NaOH}$  (w/W) means

$$\begin{aligned}
 100 \text{ g NaOH solution} &\text{ has } = 50 \text{ g NaOH} \\
 \frac{100}{1.52} \text{ mL NaOH solution} &\text{ has } = 50 \text{ g NaOH} \\
 \therefore \frac{1}{15.2} \text{ L NaOH solution} &\text{ has } = \frac{50}{40} = 1.25 \text{ mol NaOH} \\
 \therefore \text{Molarity of NaOH} &= 1.25 \times 15.2 \text{ M} \\
 &= 19 \text{ M}
 \end{aligned}$$

**Illustration 7**  $\text{HCl}$  is 80% ionised in 0.01 M aqueous solution. What is its equilibrium molarity? What are other species present? What are their molar concentrations?

**Solution** Initial  $[\text{HCl}] = 0.01 \text{ M}$



Equilibrium molarity

$$\begin{aligned}
 [\text{HCl}] &= 0.010 - 0.008 = 0.002 \text{ M} \\
 [\text{H}_3\text{O}^+] &= 0.008 \text{ M} \\
 [\text{Cl}^-] &= 0.008 \text{ M}
 \end{aligned}$$

**Illustration 8** What is molarity of  $\text{K}^+$  in aqueous solution that contains 17.4 ppm  $\text{K}_2\text{SO}_4$  ( $174 \text{ g mol}^{-1}$ )

**Solution**  $\text{K}_2\text{SO}_4$  is 17.4 ppm i.e.,

$$\begin{aligned}
 10^6 \text{ g (}\approx \text{ mL)} \text{ solution} &\text{ has } = 17.4 \text{ g } \text{K}_2\text{SO}_4 \\
 10^3 \text{ mL solution} &\text{ has } = \frac{17.4 \times 10^3}{10^6} \text{ g } \text{K}_2\text{SO}_4 \\
 &= 0.0174 \text{ g L}^{-1} \text{K}_2\text{SO}_4 \\
 \therefore [\text{K}_2\text{SO}_4] &= \frac{0.0174}{174} = 1 \times 10^{-4} \text{ M} \\
 \text{K}_2\text{SO}_4 &\rightleftharpoons 2\text{K}^+ + \text{SO}_4^{2-} \\
 \therefore \text{Molarity of } \text{K}^+ &= 2 \times 10^{-4} \text{ M}
 \end{aligned}$$

**Illustration 9** How many millimoles of solute are contained in

- (a) 2.00 L of  $2.76 \times 10^{-3} \text{ M KMnO}_4$ ?  
 (b) 250 mL of a solution that contains 4.20 ppm  $\text{CuSO}_4$ ?

**Solution** (a) Since,

$$\begin{aligned}
 \text{volume in mL} \times \text{molarity} &= \text{millimol} \\
 \therefore 2.00 \text{ L (} = 2000 \text{ mL)} \text{ of } 2.76 \times 10^{-3} \text{ M KMnO}_4 \\
 &= 2.76 \times 10^{-3} \times 2000 \\
 &= 5.52 \text{ millimol}
 \end{aligned}$$

(b) 4.20 ppm means  $10^6$  mL solution has 4.20 g  $\text{CuSO}_4$

$$\begin{aligned}
 &= \frac{4.20}{159.5} \text{ mol} \\
 \text{hence, } 250 \text{ mL solution} &\text{ has } = \frac{4.20}{159.5} \times \frac{250}{10^6} \text{ mol } \text{CuSO}_4 \\
 &= 6.58 \times 10^{-6} \text{ mol} \\
 &= 6.58 \times 10^{-3} \text{ millimol}
 \end{aligned}$$

## Molality (m)

- The molality of a solution is defined as the number of moles of solute per kilogram of solvent ( $\text{mol kg}^{-1}$ )

$$\text{Molality (m)} = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

- The main advantage of using molality is that it is temperature independent because masses do not change when substances are heated or cooled.
- The disadvantages of using molality are that amount of solutions are measured by mass rather than by volume and that the density of the solution must be known to convert molality into molarity.

## DEEP Focus

- Molality ( $m$ ) is related to molarity ( $M$ ) by relation

$$m = \frac{1000M}{1000d - Mm_1}$$

where  $d$  is the density ( $\text{g mL}^{-1}$ ) and  $m_1$  is the molar mass of the solute

Because the density of water at 25°C is about 1 kilogram per litre, molality is approximately equal to molarity for dilute aqueous solutions at this temperature.

**Remember!** This is only for water (solvent) and if solution is not dilute and at other temperature, this approximation is not true.

Thus, 18 M  $\text{H}_2\text{SO}_4$  ( $d = 1.8 \text{ mL}^{-1}$ ,  $m_1 = 98 \text{ g mol}^{-1}$ ) is 500 molal.

$$m = \frac{1000 \times 18}{(1000 \times 1.8 - 18 \times 98)} = 500$$

### DEEP Focus

Molality ( $m$ ) expressed in terms of mole fraction of solute ( $X_1$ ) is given by relation:

$$m = \frac{1000X_1}{(1 - X_1)m_2}$$

where  $m_2$  is the molar mass of the solvent.

**Illustration 1.** 100 g solution of urea in water has 40 g urea (molar mass =  $60 \text{ g mol}^{-1}$ ). What is molality of urea solution? What is mole fraction of urea in solution?

**Solution** Mass of urea and water = 100 g

$$\begin{aligned} \text{mass of urea} &= 40 \text{ g} \\ \text{moles of urea} &= \frac{40}{60} = \frac{2}{3} \\ &= 0.667 \text{ mol} \\ \text{mass of } \text{H}_2\text{O} &= 60 \text{ g} \\ \text{moles of } \text{H}_2\text{O} &= \frac{60}{18} = 3.333 \text{ mol} \\ \text{kg of solvent (H}_2\text{O)} &= \frac{60}{1000} = 0.06 \text{ kg} \\ \text{molality (m)} &= \frac{\text{moles of urea}}{\text{kg of H}_2\text{O}} = \frac{0.667}{0.06} \\ &= 11.12 \text{ molal} \end{aligned}$$

Total moles of urea and water =  $3.333 + 0.667 = 4.00$

$$\therefore \text{mole fraction of urea} = \frac{0.667}{4.00} = 0.167$$

**Alternatively**

If molality of urea solution is  $11.12 \text{ mol kg}^{-1}$  then using relation:

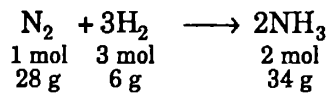
$$\begin{aligned} \text{molality (m)} &= \frac{1000X_1}{(1 - X_1)m_2} \\ 11.12 &= \frac{1000X_1}{(1 - X_1)18} \\ \frac{1 - X_1}{X_1} &= \frac{1000}{11.12 \times 18} = 5 \\ \frac{1}{X_1} &= 1 + 5 = 6 \\ X_1 &= \frac{1}{6} = 0.167 \end{aligned}$$

## Equivalent Mass and Normality

### Equivalent mass

- Equivalent mass of a substance is the mass which can combine or displace. (For more details refer unit 2 and unit 3)

1 g hydrogen  $\equiv$  8 g oxygen  $\equiv$  35.5 g chlorine  $\equiv$  80 g bromine  $\equiv$  127 g iodine  $\equiv$  12 g carbon  $\equiv$  17 g  $\text{OH}^-$



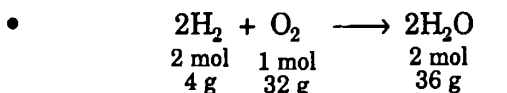
$$6 \text{ g H}_2 \equiv 28 \text{ g N}_2$$

$$1 \text{ g H}_2 \equiv \frac{28}{6} \text{ g N}_2$$

$$\therefore \text{equivalent mass of N}_2 = \frac{14}{3} \text{ g equiv}^{-1}$$

Similarly, equivalent mass of

$$\text{NH}_3 = \frac{34}{6} = \frac{17}{3} \text{ g equiv}^{-1}$$



$$32 \text{ g O}_2 \equiv 36 \text{ g H}_2\text{O}$$

$$\therefore 8 \text{ g O}_2 \equiv 9 \text{ g H}_2\text{O}$$

Thus, equivalent mass of  $\text{H}_2\text{O} = 9 \text{ g}$

(determined w.r.t. oxygen)

$$\text{Also, } 4 \text{ g H}_2 \equiv 36 \text{ g H}_2\text{O}$$

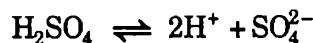
$$1 \text{ g H}_2 \equiv 9 \text{ g H}_2\text{O}$$

Thus, w.r.t. hydrogen equivalent mass of  $\text{H}_2\text{O}$  is also  $9 \text{ g equiv}^{-1}$

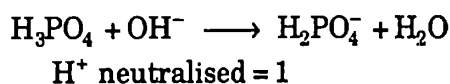
$$\bullet \text{ Number of equivalent} = \frac{\text{mass}}{\text{equivalent mass}}$$

**Normality (N)** Concentration of the solution expressed in number of equivalent dissolved per litre of solution is called normality.

An equivalent is a measure of the reactive capacity of a given molecule. **Normality is the only concentration unit that is reaction dependent.** 1 M sulphuric acid is 2 N for acid-base reactions because each mole of sulphuric acid produce 2 moles of  $\text{H}^+$  ions. On the other hand, 1 M sulphuric acid is 1 N for sulphate ion, since 1 mole sulphuric acid provides one mole of sulphate ion.

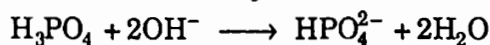


$\text{H}_3\text{PO}_4$  (ortho phosphoric acid) can be neutralised stepwise in three steps and depending upon the number of  $\text{H}^+$  ions neutralised, normality would be different (say we take 1 M  $\text{H}_3\text{PO}_4$ )



$$\text{Equivalent mass} = \frac{\text{molar mass}}{1}$$

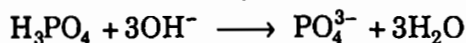
$$\text{Normality} = 1 \text{ N}$$



$$\text{H}^+ \text{ neutralised} = 2$$

$$\text{Equivalent mass} = \frac{\text{molar mass}}{2}$$

$$\text{Normality} = 2 \text{ N}$$



$$\text{H}^+ \text{ neutralised} = 3$$

$$\text{Equivalent mass} = \frac{\text{molar mass}}{3}$$

$$\text{Normality} = 3 \text{ N}$$

$$\text{Normality (N)} = \frac{\text{number of equivalent}}{\text{litre of solution}}$$

If 0.40 g NaOH is dissolved in 100 mL (= 0.1 L) solution,

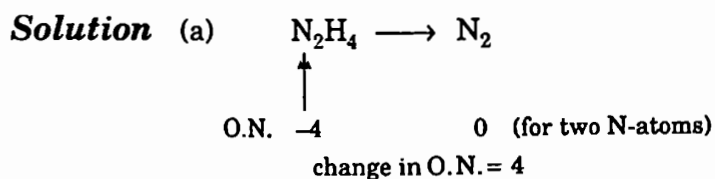
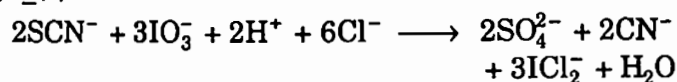
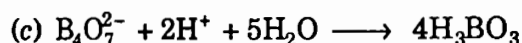
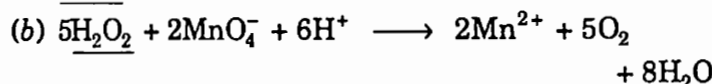
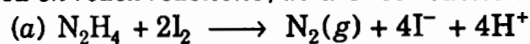
$$\text{then, number of equivalent of NaOH} = \frac{0.40}{40} = 0.01$$

$$\therefore \text{normality of NaOH solution} = \frac{0.01}{0.10} = 0.1 \text{ N}$$

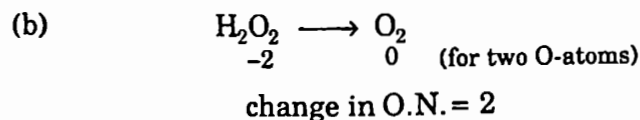
$$\text{Also, } NV = \text{milliequivalent (x)} = \frac{x}{1000} \text{ equivalent.}$$

$$NE = \text{concentration in g L}^{-1}.$$

**Illustration 1** Calculate equivalents of the underlined based on redox reactions/acid-base reactions.



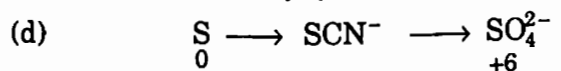
$$\therefore 1 \text{ mol N}_2\text{H}_4 = 4 \text{ equivalents N}_2\text{H}_4$$



$$\therefore 1 \text{ mol H}_2\text{O}_2 = 2 \text{ equivalents H}_2\text{O}_2$$

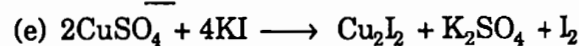
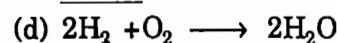
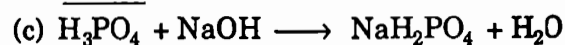
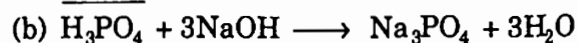
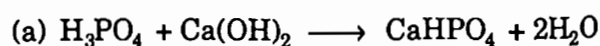


$$\therefore 1 \text{ mol B}_4\text{O}_7^{2-} = 2 \text{ equivalents}$$

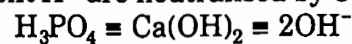


$$1 \text{ mol S} = 6 \text{ equivalents of S}$$

**Illustration 2** Determine equivalent mass of the underlined:

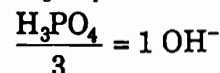


**Solution** (a)  $\text{H}_3\text{PO}_4$  is a tribasic acid but in this case only two equivalent  $\text{H}^+$  are neutralised by  $\text{Ca}(\text{OH})_2$ .

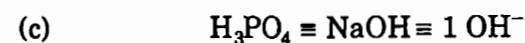


$$\therefore 1 \text{ OH}^- = \frac{\text{H}_3\text{PO}_4}{2}$$

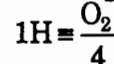
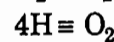
$$\text{Thus, equivalent mass of H}_3\text{PO}_4 = \frac{\text{molar mass}}{2} = \frac{98}{2} = 49 \text{ g equiv}^{-1}$$



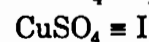
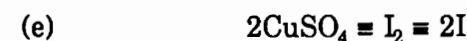
$$\text{equivalent mass of H}_3\text{PO}_4 = \frac{98}{3} \text{ g equiv}^{-1}$$



$$\text{equivalent mass of H}_3\text{PO}_4 = 98 \text{ g equiv}^{-1}$$



$$\therefore \text{equivalent mass of O}_2 = \frac{\text{molar mass}}{4} = 8 \text{ g equiv}^{-1}$$



$$\text{equivalent mass of CuSO}_4 = \text{molar mass} = 159.5 \text{ g equiv}^{-1}$$

**Illustration 3** At a given condition, 1 mole of  $\text{O}_2$  occupies volume 30 L. What is volume occupied by 1 equivalent of  $\text{O}_2$ ?

$$\text{Solution} \quad \text{Molar mass of O}_2 (= 1 \text{ mol}) = 32 \text{ g}$$

$$\text{equivalent mass of O}_2 = 8 \text{ g}$$

$$\text{hence, } 1 \text{ mol O}_2 = 4 \text{ equivalent O}_2$$

$$\text{If } 1 \text{ mol O}_2 \text{ occupies} = 30 \text{ L}$$

$$\text{then } 1 \text{ equivalent O}_2 \text{ occupies} = \frac{30}{4} = 7.5 \text{ L}$$

**Illustration 4** 0.024 g of Mg on burning in oxygen gave 0.40 g of  $\text{MgO}$ . What is equivalent mass of Mg?

**Solution** Mass of Mg = 0.24 g, mass of  $\text{MgO}$  = 0.40 g  
oxygen combined = 0.16 g

$$\therefore 0.16 \text{ g oxygen} = 0.24 \text{ g Mg}$$

$$\therefore 8 \text{ g oxygen} = 12 \text{ g Mg}$$

$$\text{Thus, equivalent mass of Mg} = 12 \text{ g equiv}^{-1}$$

**Illustration 5** When 6 g of a monobasic acid is dissolved in 100 mL solution, it is 1 N. What is equivalent mass of the acid?

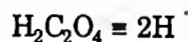
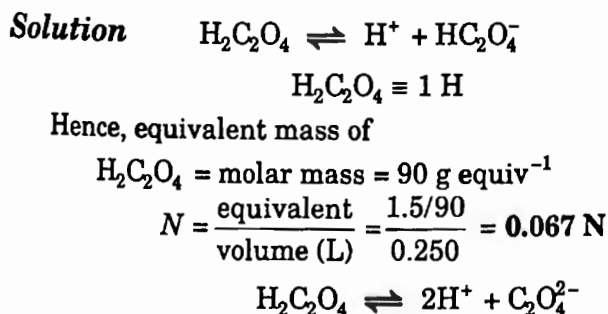
**Solution** Normality =  $\frac{\text{equivalent of substance}}{\text{litre of solution}}$

$$1 \text{ N} = \frac{6}{E/0.1}$$

$$\frac{6}{E} = 0.1$$

$$E = 60 \text{ g equiv}^{-1}$$

**Illustration 6** Oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , forms two series of salt  $\text{HC}_2\text{O}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$ . 1.5 g of  $\text{H}_2\text{C}_2\text{O}_4$  is dissolved in 250 mL solution. Determine its normality at each stage of salt formation.



$\therefore$  Equivalent mass of

$$\text{H}_2\text{C}_2\text{O}_4 = \frac{\text{molar mass}}{2} = 45 \text{ g equiv}^{-1}$$

$$N = \frac{1.5/45}{0.250} = 0.133 \text{ N}$$

**Illustration 7** 10 g of  $\text{MnO}_2$  on reaction with conc. HCl liberated 0.1 equivalent of  $\text{Cl}_2$ . What is per cent purity of  $\text{MnO}_2$ ? (Mn = 55, O = 16, Cl = 35.5)



**Solution**

$$\begin{array}{l} \text{MnO}_2 \equiv \text{Cl}_2 \\ 87 \text{ g} \quad 71 \text{ g} \\ \text{MnO}_2 \equiv \text{Cl}_2 \equiv 2\text{Cl} \\ 1 \text{ Cl} = \frac{\text{MnO}_2}{2} = \frac{87}{2} = 43.5 \text{ g} \\ \therefore 1 \text{ equivalent of } \text{Cl}_2 = 43.5 \text{ g MnO}_2 \\ 0.1 \text{ equivalent of } \text{Cl}_2 = 4.35 \text{ g MnO}_2 \text{ (pure)} \\ \text{But, MnO}_2 \text{ taken} = 10 \text{ g} \\ \therefore \text{percentage of pure MnO}_2 = \frac{4.35}{10} \times 100 = 43.5\% \end{array}$$

## Target Practice 1

- How many grams of  $\text{Na}^+$  are contained in 25 mL of 1 M  $\text{Na}_2\text{SO}_4$  .....
- How many moles and millimoles of benzoic acid are contained in 10 mL of 0.5 M benzoic acid .....
- Calculate molar concentration of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) in an aqueous solution that contains 2.3 g of  $\text{C}_2\text{H}_5\text{OH}$  in 3.5 L solution .....
- Describe preparation of 2.00 L of 0.108 M  $\text{BaCl}_2$  from  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  (Ba = 137) .....
- Describe the preparation of 500 mL of 0.01 M  $\text{Cl}^-$  solution from solid  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  (Ba = 137) .....
- Calculate the resulting molarity when 145 mL of 6.00 M  $\text{H}_2\text{SO}_4$  is mixed with 245 mL of 3.00 M  $\text{H}_2\text{SO}_4$  .....
- A solution contains 0.10 mole per litre of each of the following acids:  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ .
  - Is the molarity the same for each acid? .....
  - Is the number of molecules per litre the same for each acid? .....
  - Is the normality the same for each acid? .....
- Calculate the volume of 0.0600 M  $\text{Ba(OH)}_2$  solution that contains the same number of moles of  $\text{Ba(OH)}_2$  as 180 mL of 0.09 M  $\text{Ba(OH)}_2$  solution? .....

- Calculate the volume of 4.00 M NaOH solution required to prepare 200 mL of a 0.750 M solution of NaOH .....
- Complete the table for the following aqueous solution

|     | Solute                  | Mass solute (g) | Volume (litres) | Molarity |
|-----|-------------------------|-----------------|-----------------|----------|
| (a) | HCl                     | 0.365           | 0.01            | (I) ...  |
| (b) | $\text{H}_2\text{SO}_4$ | 0.98            | (II) ...        | 1.0      |
| (c) | $\text{H}_3\text{PO}_4$ | (III) ...       | 1.00            | 0.1      |
| (d) | NaOH                    | (IV) ...        | 2.00            | 0.25     |
| (e) | $\text{Ca(OH)}_2$       | 7.40            | 1.00            | (V) ...  |

- What is normality if molarity of the underlined solute is 1 M?
  - $\underline{\text{H}_3\text{PO}_4} + \text{Ca(OH)}_2 \longrightarrow \text{CaHPO}_4 + 2\text{H}_2\text{O}$  .....
  - $\underline{\text{H}_3\text{PO}_3} + \text{NaOH} \longrightarrow \text{NaH}_2\text{PO}_3 + \text{H}_2\text{O}$  .....
  - $\underline{\text{H}_3\text{PO}_2} + \text{Ca(OH)}_2 \longrightarrow \text{Ca(OH)H}_2\text{PO}_2 + \text{H}_2\text{O}$  .....
  - $(\underline{\text{NH}_4})_2\text{SO}_4 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{NH}_3 + 2\text{H}_2\text{O}$  .....
  - $\underline{\text{Ba(OH)}}_2 + 2\text{HCl} \longrightarrow \text{BaCl}_2 + 2\text{H}_2\text{O}$  .....

## Answers



One mole furnishes two moles of  $\text{Na}^+$  ions

$$\begin{aligned} \text{millimoles} &= \text{volume (mL)} \times \text{molarity} \\ &= 25 \times 1 \end{aligned}$$

$$= 25 \text{ millimol of } \text{Na}_2\text{SO}_4$$

$$= 50 \text{ millimol of } \text{Na}^+$$

$$\therefore \text{Moles of } \text{Na}^+ = \frac{50}{1000} = 0.050$$

$$\text{Mole} \times \text{molar mass} = 0.050 \times 23 = 1.15 \text{ g Na}^+$$



2. Benzoic acid =  $10 \times 0.5$  millimol  
 $= 5$  millimol = 0.005 mol

3. Molarity =  $\frac{\text{moles}}{\text{volume in litre}}$

$2.3 \text{ g C}_2\text{H}_5\text{OH} = \frac{2.3}{46} = 0.05 \text{ mol}$

$\therefore \text{Molarity} = \frac{0.05}{3.5} = 0.0143 \text{ mol L}^{-1}$

4.  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O} = 2 \times 0.108$   
 $= 0.216 \text{ mol}$   
 $= 0.216 \times 244 \text{ g}$   
 $= 52.704 \text{ g}$

We dissolve 52.704 g  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in 2.00 L solution

5.  $0.01 \text{ M Cl}^- = \frac{0.01}{2} \text{ M BaCl}_2 \cdot 2\text{H}_2\text{O}$   
 $= 0.005 \text{ M BaCl}_2 \cdot 2\text{H}_2\text{O}$   
 $= 0.005 \text{ mol L}^{-1} \text{ BaCl}_2 \cdot 2\text{H}_2\text{O}$   
 $= 0.0025 \text{ mol in } 500 \text{ mL}$

Dissolve 0.0025 mol (= 0.61 g)  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in 500 mL solution.

6. Resulting molarity =  $\frac{\Sigma MV}{\Sigma V}$   
 $= \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$   
 $= \frac{6 \times 145 + 3 \times 245}{145 + 245}$   
 $= 4.0125 \text{ M}$

7. Molarity =  $\frac{\text{Mol}}{\text{L}}$

|     | HCl              | H <sub>2</sub> SO <sub>4</sub> | H <sub>3</sub> PO <sub>4</sub> |                    |
|-----|------------------|--------------------------------|--------------------------------|--------------------|
| (a) | 0.1 M            | 0.1 M                          | 0.1 M                          | Molarity same-Yes  |
| (b) | $0.1 \times N_0$ | $0.1 \times N_0$               | $0.1 \times N_0$               | Molecules same-Yes |
| (c) | 0.1 N            | 0.2 N                          | 0.3 N                          | Normality same-No  |

( $N_0$  = Avogadro's number)

8. It is a case of dilution

$$M_1 V_1 = M_2 V_2$$

$$0.06 \times V_1 = 0.09 \times 180$$

$$V_1 = 270 \text{ mL}$$

9. It is a case of dilution

$$M_1 V_1 = M_2 V_2$$

$$4 \times V_1 = 0.75 \times 200$$

$$V_1 = 37.5 \text{ mL}$$

10. I — 1 M  
 II — 0.01 L  
 III — 9.8 g  
 IV — 20.0 g  
 V — 0.1 M

|                                                                                                            | Normality |
|------------------------------------------------------------------------------------------------------------|-----------|
| 11. (a) Two H <sup>+</sup> ions are neutralised                                                            | — 2 N     |
| (b) One H <sup>+</sup> ion is neutralised                                                                  | — 1 N     |
| (c) One H <sup>+</sup> ion is neutralised                                                                  | — 1 N     |
| (d) One mole (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> is neutralised by two (OH <sup>-</sup> ) ions | — 2 N     |
| (e) One mole Ba(OH) <sub>2</sub> is neutralised by two HCl                                                 | — 2 N     |

## Practice Exercise 1

- How many equivalents of hydrogen are in 1 equivalent of H<sub>3</sub>PO<sub>4</sub>?
- 0.400 g of iron (III) sulphate are present in 100 mL of solution. Express concentration of iron (III) and sulphate ions in terms of  
 (i) ppm (ii) molarity
- H<sub>2</sub>SO<sub>4</sub> ( $d = 1.80 \text{ g mL}^{-1}$ ) is 98% by weight of solution. Express concentration in terms of molarity of  
 (i) hydrogen ion, (ii) sulphate ion
- $\text{MCl}_x$  is 100% ionised in 0.01 M aqueous solution. If  $[\text{Cl}^-] = 0.03 \text{ M}$ , what is the formula? Also calculate  $[M^{x+}]$  and  $[\text{MCl}_x]$ .
- A solution of Na<sub>2</sub>SO<sub>4</sub> is 50% ionised. What is analytical molarity of Na<sub>2</sub>SO<sub>4</sub> if  $[\text{Na}^+] = 1.0 \text{ M}$ ?
- 6 g of an urea sample (molar mass = 60 g mol<sup>-1</sup>) was dissolved in 100 mL aqueous solution and was 0.8 M. Comment.
- The same amount of a metal combines with 0.4 g of oxygen and 4 g of a halogen. Determine equivalent mass of halogen.
- (a) The equivalent mass of a metal is double that of oxygen. How many times is the mass of its oxide greater than the mass of the metal?  
 (b) 1.575 g of a dibasic acid H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> · xH<sub>2</sub>O in 250 mL solution is 0.1 N. What is the value of x?
- Urea solution is 20% by weight of solution. What is percentage concentration by weight of solvent?
- Calculate normality of:  
 (a) 0.01 M Ba(OH)<sub>2</sub> (b) 0.01 M H<sub>3</sub>PO<sub>3</sub>  
 (c) 0.01 M H<sub>3</sub>PO<sub>2</sub> (d) 0.01 M H<sub>3</sub>PO<sub>4</sub> solutions.
- What is weight of sucrose in 1 kg solution of 1 mole concentration?
- One litre of 1 M solution of following are to be prepared. Which has maximum weight of solute?  
 (Mn = 55, K = 39, Cr = 52, Fe = 56)  
 (a) KMnO<sub>4</sub> (b) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>  
 (c) FeSO<sub>4</sub> · (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> · 6H<sub>2</sub>O
- 2.78 g FeSO<sub>4</sub> · xH<sub>2</sub>O in 100 mL solution gives 0.1 M solution. What is the value of x?
- CH<sub>3</sub>CH<sub>2</sub>OH solution in water is 46% by weight of solution. What is mole fraction of each component? What is molality as water solvent? What is molality as ethanol solvent?
- Calculate volume of water that must be added to 250 mL of 1.25 N solution to make it 0.500 N.
- What volumes of 12.0 N and 3.00 N HCl must be mixed to give 1.00 L of 6.00 N HCl?



1342 g solution has sucrose = 342 g

Thus, 1000 g solution has sucrose =  $\frac{342}{1342} \times 1000 = 254.84$  g

12.

| Solute                                                                                  | Molecular weight        | Moles in one litre of 1 M solution |
|-----------------------------------------------------------------------------------------|-------------------------|------------------------------------|
| KMnO <sub>4</sub>                                                                       | 158 g mol <sup>-1</sup> | 1 mol                              |
| K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>                                           | 294 g mol <sup>-1</sup> | 1 mol                              |
| FeSO <sub>4</sub> · (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> · 6H <sub>2</sub> O | 392 g mol <sup>-1</sup> | 1 mol                              |

Thus, maximum weight is of FeSO<sub>4</sub> · (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> · 6H<sub>2</sub>O

13. Molar mass of FeSO<sub>4</sub> · xH<sub>2</sub>O = 152 + 18x

$$\text{Moles of FeSO}_4 \cdot x\text{H}_2\text{O} = \frac{2.78}{(152 + 18x)}$$

$$\text{Volume} = 100 \text{ mL} = 0.1 \text{ L}$$

$$\text{Molarity} = \frac{2.78/(152 + 18x)}{0.1}$$

$$\text{Thus, } \frac{2.78}{152 + 18x} / 0.1 = 0.1 \text{ (given)}$$

$$\therefore x = 7$$

14. CH<sub>3</sub>CH<sub>2</sub>OH = 46% by weight of solution

Thus, CH<sub>3</sub>CH<sub>2</sub>OH = 46 g = 1 mol = 0.046 kg

H<sub>2</sub>O = 54 g = 3 mol = 0.054 kg

Total moles = 4

Mole fraction of CH<sub>3</sub>CH<sub>2</sub>OH =  $X_{\text{CH}_3\text{CH}_2\text{OH}} = \frac{1}{4}$

Mole fraction of H<sub>2</sub>O =  $X_{\text{H}_2\text{O}} = \frac{3}{4}$

$$\begin{aligned} \text{Molality as water solvent} &= \frac{\text{mole of solute (CH}_3\text{CH}_2\text{OH)}}{\text{kg of solvent (H}_2\text{O)}} \\ &= \frac{1}{0.054} \end{aligned}$$

$$= 18.52 \text{ molal}$$

Molality as ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) solvent

$$\begin{aligned} &= \frac{\text{mole of solute (H}_2\text{O)}}{\text{kg of solvent (CH}_3\text{CH}_2\text{OH)}} \\ &= \frac{3}{0.046} \end{aligned}$$

$$= 65.22 \text{ molal}$$

15. It is a case of dilution :

$$\begin{aligned} N_1 V_1 &= N_2 V_2 \\ 0.5 \times V_1 &= 1.25 \times 250 \\ V_1 &= 625 \text{ mL} \end{aligned}$$

$$\begin{aligned} \text{Thus, additional water to be added} &= 625 - 250 \\ &= 375 \text{ mL} \end{aligned}$$

16. If volume of 12.00 N HCl = x L

then volume of 3.00 N = (1 - x) L

Final normality = 6.00 N

$$N \text{ (final)} = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

$$6 = \frac{12x + 3(1 - x)}{1}$$

$$x = 0.333 \text{ L}$$

Thus, volume of 12 N HCl = 0.333 L

and volume of 3 N HCl = 0.667 L

## Volumetric Titrations

While diluting a solution from one concentration to another, we can use

$$M_1 V_1 = M_2 V_2$$

and

$$N_1 V_1 = N_2 V_2$$

(concentrated solution) (diluted solution)

- For a redox reaction or neutralisation reaction

$$N_1 V_1 = N_2 V_2 \text{ is always true}$$

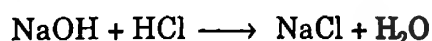
but  $M_1 V_1 = M_2 V_2$  is not always true

- Normality = change in O.N. × molarity in a redox reaction

(O.N. = oxidation number)

- Normality = molarity × basicity (of an acid)

$$= \text{molarity} \times \text{acidity (of a base)}$$

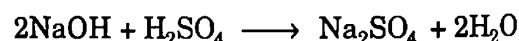


Here,

$$N_1 V_1 = N_2 V_2$$

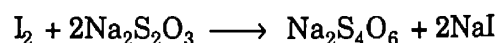
and also

$$M_1 V_1 = M_2 V_2$$



$$\text{Here, } N_1 V_1 (\text{NaOH}) = N_2 V_2 (\text{H}_2\text{SO}_4)$$

$$\text{but } M_1 V_1 (\text{NaOH}) = 2M_2 V_2 (\text{H}_2\text{SO}_4)$$



$$N_1 V_1 (\text{I}_2) = N_2 V_2 (\text{Na}_2\text{S}_2\text{O}_3)$$

$$\text{but } 2M_1 V_1 (\text{I}_2) = M_2 V_2 (\text{Na}_2\text{S}_2\text{O}_3)$$

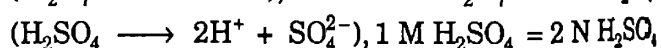


$$\text{Here, } N_1 V_1 (\text{Fe}^{2+}) = N_2 V_2 (\text{MnO}_4^-)$$

$$\text{but } M_1 V_1 (\text{Fe}^{2+}) = 5M_2 V_2 (\text{MnO}_4^-)$$

### DEEP Focus

Thus, it is always better to convert molarity factor into normality factor by multiplying it with change in O.N. or acidity or basicity.



- Normality of a mixture of two or more acids or bases (strong)

$$N_{\text{mix}} = \frac{N_1 V_1 + N_2 V_2 + \dots}{V_1 + V_2 + \dots} = \frac{\Sigma NV}{\Sigma V}$$

where  $N_1, N_2, \dots$  are normalities and  $V_1, V_2, \dots$  are volumes of acids or bases.

- Normality of mixture of acid and bases (strong)

let  $N_1 V_1$  = milliequivalent of acid

$N_2 V_2$  = milliequivalent of base

- If  $N_1 V_1 = N_2 V_2$  mixture is **neutral**

- If  $N_1 V_1 > N_2 V_2$ , then mixture is **acidic** and resultant normality of acidic solution is:

$$N(\text{resultant}) = \frac{N_1 V_1 - N_2 V_2}{V_1 + V_2}$$

- If  $N_1 V_1 < N_2 V_2$ , then mixture is **basic** and resultant normality of basic solution is:

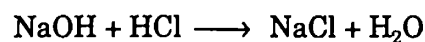
$$N(\text{resultant}) = \frac{N_2 V_2 - N_1 V_1}{V_1 + V_2}$$

- In all cases : equivalent of an acid = equivalent of a base

- When neutralisation point is reached  $N_1 V_1 = N_2 V_2$

*End point is the point of completion of the reaction indicated by suitable indicator. Hence, it has additional drop of titrating reagent but, we use*

$$N_1 V_1 = N_2 V_2$$

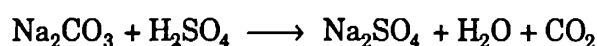
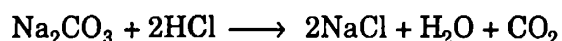


1 equivalent of NaOH  $\equiv$  1 equivalent of HCl

$\equiv$  1 mol of HCl

$\equiv$  1 equivalent of  $\text{H}_2\text{SO}_4$

$\equiv$  0.5 mol of  $\text{H}_2\text{SO}_4$



1 equivalent of  $\text{Na}_2\text{CO}_3 \equiv$  0.5 mol of  $\text{Na}_2\text{CO}_3$

$\equiv$  1 equivalent of HCl

$\equiv$  1 mol of HCl

$\equiv$  1 equivalent of  $\text{H}_2\text{SO}_4$

$\equiv$  0.5 mol of  $\text{H}_2\text{SO}_4$

## Acid-Base Titrations

Acid or acid mixture can be titrated against a suitable base or *vice-versa* using a suitable indicator. These are summarised in Table 7.3

Table 7.3 Acid-Base Titrations

| Combination                    | Suitable indicator                | Colour change |                |
|--------------------------------|-----------------------------------|---------------|----------------|
|                                |                                   | in acid       | in alkali      |
| 1. Strong acid/<br>strong base | Methyl orange<br>Bromothymol blue | Red<br>Yellow | Yellow<br>Blue |
| 2. Strong acid/<br>weak base   | Methyl red                        | Red           | Yellow         |
| 3. Weak acid/<br>strong base   | Phenolphthalein                   | Colourless    | Purple         |
| 4. Weak acid/<br>weak base     | Not suitable for a<br>titration   |               |                |

Extent of reaction of different bases with acid (HCl) using these two indicators is summarised below :

| Mixture                  | Phenolphthalein                                                                                                                              | Methyl orange                                                                                                                         |
|--------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------|
| NaOH                     | 100% reaction is indicated<br>$\text{NaOH} + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O}$                                    | 100% reaction is indicated,<br>$\text{NaOH} + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O}$                            |
| $\text{Na}_2\text{CO}_3$ | 50% reaction up to $\text{NaHCO}_3$ stage is indicated<br>$\text{Na}_2\text{CO}_3 + \text{HCl} \longrightarrow \text{NaHCO}_3 + \text{NaCl}$ | 100% reaction is indicated,<br>$\text{Na}_2\text{CO}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$ |
| $\text{NaHCO}_3$         | No reaction is indicated                                                                                                                     | 100% reaction is indicated<br>$\text{NaHCO}_3 + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$            |

Suppose volume of given standard acid solution (say HCl) required

for complete reaction of  $\text{Na}_2\text{CO}_3 = x$  mL

for complete reaction of  $\text{NaHCO}_3 = y$  mL

for complete reaction of  $\text{NaOH} = z$  mL

## Titration of Mixture of Bases with Two Indicators

Every indicator has a working range

| Indicator       | pH range | Behaving as       |
|-----------------|----------|-------------------|
| Phenolphthalein | 8–10     | weak organic acid |
| Methyl orange   | 3–4.4    | weak organic base |

Thus, methyl orange with lower pH range can indicate complete neutralisation of all types of bases.

There may be different combination of mixture of bases. We may adopt two methods:

**Method I:** We carry two titrations separately with two different indicators.

**Method II:** We carry single titration but adding second indicator after first end-point is reached.

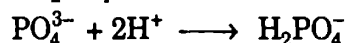
These have been summarised in Table 7.4

Table 7.4 Results with Two Indicators

| Mixture                                                 | Method I                                          |                        | Method II                                         |                                                                                                                                    |
|---------------------------------------------------------|---------------------------------------------------|------------------------|---------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|
|                                                         | Volume of HCl used with Indicator                 |                        | Volume of HCl used with Indicator                 |                                                                                                                                    |
|                                                         | Phenolphthalein                                   | Methyl orange          | Phenolphthalein                                   | Methyl orange added after first end-point is reached                                                                               |
| 1. NaOH + Na <sub>2</sub> CO <sub>3</sub>               | $\left(z + \frac{x}{2}\right)$<br>↑ ↑<br>100% 50% | $(x + z)$<br>100% each | $\left(z + \frac{x}{2}\right)$<br>↑ ↑<br>100% 50% | $\frac{x}{2}$<br>(remaining 50% Na <sub>2</sub> CO <sub>3</sub> is indicated)                                                      |
| 2. NaOH + NaHCO <sub>3</sub>                            | $z + 0$<br>100% no change                         | $(y + z)$<br>100% each | $(z + 0)$                                         | $y$ (remaining 100% NaHCO <sub>3</sub> is indicated)                                                                               |
| 3. Na <sub>2</sub> CO <sub>3</sub> + NaHCO <sub>3</sub> | $\frac{x}{2} + 0$<br>↑ ↑<br>50% no change         | $(x + y)$<br>100% each | $\left(\frac{x}{2} + 0\right)$                    | $\left(\frac{x}{2} + y\right)$<br>(remaining 50% of Na <sub>2</sub> CO <sub>3</sub> and 100% of NaHCO <sub>3</sub> are indicated.) |

- Bromocresol-green also indicates complete reaction of Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub> and NaOH, thus its behaviour is similar to methyl orange.

- Bromocresol can also be used as an indicator for the determination of phosphates when reaction of acid (say HCl) up to H<sub>2</sub>PO<sub>4</sub><sup>-</sup> is indicated.



- Thymolphthalein indicates reaction upto the formation of HPO<sub>4</sub><sup>2-</sup>.

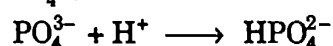


**Illustration 1** Calculate the molar concentration of a dilute HCl solution if

(a) titration of a 50 mL of 0.04 M Ba(OH)<sub>2</sub> required 20 mL of the acid.

(b) 50 mL of HCl yielded 0.6010 g AgCl

**Solution** (a)  $\text{Ba}(\text{OH})_2 + 2\text{HCl} \longrightarrow \text{BaCl}_2 + 2\text{H}_2\text{O}$

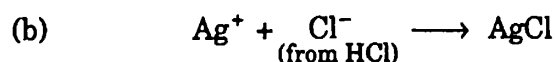
$$0.04 \text{ M Ba}(\text{OH})_2 = 0.08 \text{ N Ba}(\text{OH})_2$$

$$\frac{N_1 V_1}{\text{HCl}} = \frac{N_2 V_2}{\text{Ba}(\text{OH})_2}$$

$$N_1 \times 20 = 0.08 \times 50$$

$$N_1(\text{HCl}) = 0.20 \text{ N}$$

$$\therefore \text{molar concentration} = 0.20 \text{ M}$$



$$\begin{array}{ccc} 1 \text{ mol} & 1 \text{ mol} = 143.5 \text{ g} \\ ? & 0.6010 \text{ g} \end{array}$$

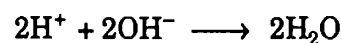
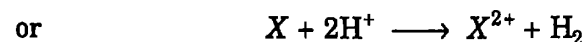
$$143.5 \text{ g AgCl is obtained from} = 1 \text{ mol HCl}$$

$$\begin{aligned} \therefore 0.6010 \text{ g AgCl is obtained from} &= \frac{0.6010}{143.5} \text{ mol HCl} \\ &= 4.188 \times 10^{-3} \text{ mol HCl} \end{aligned}$$

This amount of HCl is contained in 50 mL solution (= 0.050 L)

$$\begin{aligned} \therefore \text{molar concentration of HCl} &= \frac{4.188 \times 10^{-3}}{0.050} \\ &= 0.08376 \text{ M} \end{aligned}$$

**Illustration 2** A 1.00 g sample of a metal X (that is known to form X<sup>2+</sup> ions) was added to 0.10 L of 0.50 M H<sub>2</sub>SO<sub>4</sub>. After all the metal had reacted, the remaining acid required 0.0334 L of 0.50 M NaOH solution for neutralisation. Calculate molar mass of the metal and identify the element.



$$1 \text{ mol H}_2\text{SO}_4 \equiv 1 \text{ mol of X} = \text{molar mass of X}$$

Let unused acid = V L

then V L of 0.5 M H<sub>2</sub>SO<sub>4</sub>  $\equiv$  0.0334 L of 0.5 M NaOH

or V L of 1 N H<sub>2</sub>SO<sub>4</sub>  $\equiv$  0.0334 L of 0.5 N NaOH

$$\therefore V = 0.0167 \text{ L of H}_2\text{SO}_4$$

$$\text{H}_2\text{SO}_4 \text{ used} = 0.10 - 0.0167 = 0.0833 \text{ L}$$

$$\begin{aligned} \text{Number of moles of H}_2\text{SO}_4 &= 0.0833 \times 0.5 \text{ mol} \\ &= 1 \text{ g metal X} \end{aligned}$$

$$\therefore 1 \text{ mol of H}_2\text{SO}_4 = \frac{1}{0.0833 \times 0.5} \text{ g metal X}$$

$$= 24.01 \text{ g mol}^{-1}$$

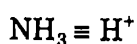
Metal is **Mg**.

**Note:** This is a case of **back-titration**.

## Kjeldahl Method

Kjeldahl method is used to determine amount of N-containing compounds as  $\text{NH}_3$ ,  $\text{NH}_2\text{CONH}_2$ ,  $\text{NH}_4\text{Cl}$ , etc. Compound is decomposed by alkali ( $\text{NaOH}$ ,  $\text{Ca}(\text{OH})_2$ , etc.) and  $\text{NH}_3$  formed is absorbed by excess of standard  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  solution. Unreacted acid is determined by **back-titration**.

If  $V$  is the volume of acid or normality ( $N$ ) required to absorb  $\text{NH}_3$  from  $w$  g of the compound then,



$$\text{Equivalent of acid} \equiv \text{equivalent of NH}_3 = \frac{NV}{1000}$$

$$\text{NH}_3 \text{ present} = \frac{17NV}{1000} \text{ g}$$

$$w \text{ g of the compound has} = \frac{17NV}{1000} \text{ g NH}_3$$

$$100 \text{ g of the compound has} = \frac{17NV \times 100}{1000w} \text{ NH}_3$$

$$\% \text{ of NH}_3 = \frac{1.7 NV}{w}$$

$$\% \text{ in terms of N} = \frac{1.4 NV}{w} \text{ since } \text{N} \equiv \text{NH}_3 \equiv \text{H}^+$$

$$\% \text{ in terms of NH}_4\text{Cl} = \frac{5.35 NV}{w} \text{ since } \text{NH}_4\text{Cl} \equiv \text{NH}_3 \equiv \text{H}^+$$

$$\% \text{ in terms of (NH}_4)_2\text{SO}_4 = \frac{6.6 NV}{w}$$

$$\text{since } (\text{NH}_4)_2\text{SO}_4 \equiv 2\text{NH}_3 \equiv 2\text{H}^+$$

$$\% \text{ in terms of NH}_2\text{CONH}_2 = \frac{3.0 NV}{w}$$

$$\text{since } \text{NH}_2\text{CONH}_2 \equiv 2\text{NH}_3 \equiv 2\text{H}^+$$

**Illustration 3** A 1.047 g sample of canned tuna was analysed by the Kjeldahl method; 24.61 mL of 0.1181 M  $\text{HCl}$  were required to titrate the liberated ammonia. Calculate the percentage of nitrogen in the sample.

**Solution**  $\text{N}(\text{in the sample}) \longrightarrow \text{NH}_3 \xrightarrow{\text{HCl}} \text{NH}_4\text{Cl}$

$$\text{moles of HCl} \equiv \text{moles of NH}_3 \equiv \text{moles of N}$$

$$= \frac{24.61 \times 0.1180}{1000}$$

$$= 2.9064 \times 10^{-3}$$

$$\therefore \text{N in the given sample} = 2.9064 \times 10^{-3} \text{ mol}$$

$$= 2.9064 \times 10^{-3} \times 14 \text{ g}$$

$$= 0.0407 \text{ g}$$

$$\% \text{ of nitrogen} = \frac{0.0407}{1.047} \times 100 = 3.89\%$$

$$\text{Note: } \% \text{ of nitrogen} = \frac{1.4 NV}{w} = \frac{1.4 \times 0.1181 \times 24.61}{1.047}$$

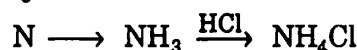
where,  $N$  = normality of acid

$V$  = volume of acid required to neutralise  $\text{NH}_3$

$w$  = weight of sample

**Illustration 4** A 0.9092 g sample of a wheat flour was analysed by the Kjeldahl procedure. The ammonia formed was distilled into 50 mL of 0.05 M  $\text{HCl}$ . A 7.50 mL of 0.05 M  $\text{NaOH}$  was required in back titration. Calculate percentage of nitrogen in the flour.

**Solution** Nitrogen content (protein) of the flour was converted into  $\text{NH}_3$  which was absorbed into  $\text{HCl}$ .



Let unreacted  $\text{HCl}$  be =  $V$  mL

$$V \text{ mL of 0.05 HCl} \equiv 7.50 \text{ mL of 0.05 M NaOH}$$

$$\therefore V = 7.50 \text{ mL}$$

$$\text{used HCl} = 50.00 - 7.50 = 42.50 \text{ mL}$$

$$\text{moles of HCl} = \text{moles of NH}_3 = \text{moles of N} = \frac{42.50 \times 0.05}{1000}$$

$$= 2.125 \times 10^{-3} \text{ mol}$$

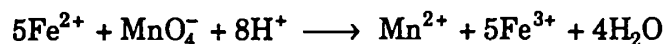
$$\therefore \text{nitrogen in the flour sample} = 2.125 \times 10^{-3} \times 14 \text{ g}$$

$$= 0.02975 \text{ g}$$

$$\% \text{ of nitrogen} = \frac{0.02975}{0.9092} \times 100 = 3.272\%$$

## Redox Titrations

Reducing agents (R.A.) like  $\text{Fe}$ ,  $\text{Fe}^{2+}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{CaOCl}_2$ ,  $\text{MnO}_2$ , etc. can be determined by suitable oxidising agents (O.A.) like  $\text{MnO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , etc. in acidic or basic or neutral medium. These are called **redox titrations**. For example,  $\text{Fe}^{2+}$  is oxidised to  $\text{Fe}^{3+}$  by  $\text{MnO}_4^-$  which in turn is reduced to  $\text{Mn}^{2+}$  in acidic medium.



Oxidising agents (O.A.) and reducing agents (R.A.) are summarised in Table 7.5.

This will certainly help to choose a particular O.A. or R.A. in a particular redox titration.

In all cases, again, we remind

$$N_1 V_1 = N_2 V_2$$

but

$$M_1 V_1 \neq M_2 V_2$$

and

$$\text{Eq. wt.} = \frac{\text{mol. wt.}}{\text{total change in O.N.}}$$

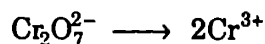
$$= \frac{\text{mol. wt.}}{\text{number of electrons gained or lost}}$$

Thus, in acidic medium  $\text{MnO}_4^-$  is changed to  $\text{Mn}^{2+}$  by gain of 5 electrons or there is change of 5 units in O.N. hence,

Eq. wt. of  $\text{MnO}_4^{2-}$  (acidic medium) =  $M/5$

Following example will certainly help, why to take total change in O.N. while determining equivalent weight

$\text{Cr}_2\text{O}_7^{2-}$  is changed to  $\text{Cr}^{3+}$

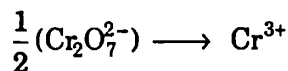


O.N. of two Cr atoms = 12 on LHS (6 per atom)

O.N. of two Cr atoms = 6 on RHS (3 per atom)

Hence, eq. wt. =  $\left(\frac{M}{6}\right)$

We can take it like this also



O.N. 6 3

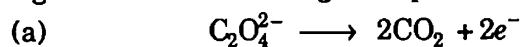
change in O.N. = 3

eq. wt. =  $\frac{(\text{formula wt. as given in equation})}{\text{change in O.N.}}$

$$= \frac{M/2}{3} = \frac{M}{6}$$

Again note this point that it will cause error in result if not considered.

Again take the following examples :



O.N. = 6 4 for two carbon atoms

change in O.N. = 2

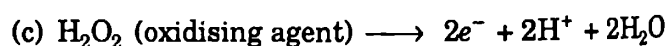
$\therefore$  eq. wt. of  $\text{C}_2\text{O}_4^{2-} = M/2$



O.N. = -2 0 for two oxygen atoms

change in O.N. = 2

eq. wt. of  $\text{H}_2\text{O}_2 = \frac{M}{2}$



O.N. = -2 -4

for two oxygen atoms

change in O.N. = 2

$\therefore$  eq. wt. of  $\text{H}_2\text{O}_2 = \frac{M}{2}$

Table 7.5 Oxidising Agents (O.A.)/Reducing Agents (R.A.) with Equivalent Weight

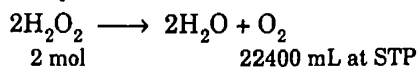
| Species                                                  | Changed to                             | Reaction                                                                                                                              | Electrons exchanged or change in O.N. | Eq. wt.                |
|----------------------------------------------------------|----------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------|------------------------|
| 1. $\text{MnO}_4^-$ (O.A.)                               | $\text{Mn}^{2+}$ in acidic medium      | $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$                                            | 5                                     | $E = \frac{M}{5}$      |
| 2. $\text{MnO}_4^-$ (O.A.)                               | $\text{MnO}_2$ in dilute basic* medium | $\text{MnO}_4^- + 3e^- + 2\text{H}_2\text{O} \longrightarrow \text{MnO}_2 + 4\text{OH}^-$                                             | 3                                     | $E = \frac{M}{3}$      |
| 3. $\text{MnO}_4^-$ (O.A.)                               | $\text{MnO}_4^{2-}$ in neutral medium  | $\text{MnO}_4^- + e^- \longrightarrow \text{MnO}_4^{2-}$                                                                              | 1                                     | $E = \frac{M}{1}$      |
| 4. $\text{Cr}_2\text{O}_7^{2-}$ (O.A.)                   | $\text{Cr}^{3+}$ in acidic medium      | $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$                              | 6                                     | $E = \frac{M}{6}$      |
| 5. $\text{MnO}_2$ (O.A.)                                 | $\text{Mn}^{2+}$ in acidic medium      | $\text{MnO}_2 + 4\text{H}^+ + 2e^- \longrightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$                                              | 2                                     | $E = \frac{M}{2}$      |
| 6. $\text{Cl}_2$ (O.A.)<br>(in bleaching powder)         | $\text{Cl}^-$                          | $\text{Cl}_2 + 2e^- \longrightarrow 2\text{Cl}^-$                                                                                     | 2                                     | $E = \frac{M}{2}$      |
| 7. $\text{CuSO}_4$ (O.A.)<br>(in iodometric titration)** | $\text{Cu}^+$                          | $\text{Cu}^{2+} + e^- \longrightarrow \text{Cu}^+$                                                                                    | 1                                     | $E = \frac{M}{1}$      |
| 8. $\text{S}_2\text{O}_3^{2-}$ (R.A.)                    | $\text{S}_4\text{O}_6^{2-}$            | $2\text{S}_2\text{O}_3^{2-} \longrightarrow \text{S}_4\text{O}_6^{2-} + 2e^-$                                                         | 2 (for two ions)                      | $E = \frac{2M}{2} = M$ |
| 9. $\text{H}_2\text{O}_2$ (O.A.)                         | $\text{H}_2\text{O}$                   | $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \longrightarrow 2\text{H}_2\text{O}$                                                       | 2                                     | $E = \frac{M}{2}$      |
| 10. $\text{H}_2\text{O}_2$ (R.A.)                        | $\text{O}_2$                           | $\text{H}_2\text{O}_2 \longrightarrow \text{O}_2 + 2\text{H}^+ + 2e^-$<br>(O.N. of oxygen in $\text{H}_2\text{O}_2$ is (-1) per atom) | 2                                     | $E = \frac{M}{2}$      |
| 11. $\text{Fe}^{2+}$ (R.A.)                              | $\text{Fe}^{3+}$                       | $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-$                                                                                 | 1                                     | $E = \frac{M}{1}$      |

\*In strong basic medium (which is not practically taken)  $4\text{MnO}_4^- + 4\text{OH}^- \longrightarrow 4\text{MnO}_4^{2-} + \text{O}_2 + 2\text{H}_2\text{O}$ ,  $E = \frac{M}{1}$

\*\*In  $\text{S}_2\text{O}_3^{2-}$ , there are two types of sulphur, terminal one with oxidation number -2 and central one with oxidation number +6, thus net value of oxidation number of +4. In  $\text{S}_4\text{O}_6^{2-}$ , oxidation number of two types of sulphur are 0 (zero) and five and thus net value of +5. When  $\text{S}_2\text{O}_3^{2-}$  is oxidised to  $\text{S}_4\text{O}_6^{2-}$ , oxidation number increase by two units for two S-atoms.

**DEEP Focus**

"Volume" concentration of  $\text{H}_2\text{O}_2$  can be expressed in terms of normality or molarity.



If  $\text{H}_2\text{O}_2$  is " $x$  volume" it means 1 mL of  $\text{H}_2\text{O}_2$  at STP gives  $x$  mL  $\text{O}_2$ .

From the above equation,

22400 mL of  $\text{O}_2$  at STP are from = 2 mol  $\text{H}_2\text{O}_2$

$$\therefore x \text{ mL } \text{O}_2 \text{ at STP are from } = \frac{2x}{22400} \text{ mol } \text{H}_2\text{O}_2$$

$$\frac{2x}{22400} \text{ mol } \text{H}_2\text{O}_2 \text{ are in 1 mL } \text{H}_2\text{O}_2 \text{ solution.}$$

$$\text{Hence, molarity of "x volume" } \text{H}_2\text{O}_2 = \frac{\text{mol}}{\text{litre}}$$

$$= \frac{2x}{22400} \times 1000 = \frac{x}{11.2} \text{ M}$$

$$\text{Normality of "x volume" } \text{H}_2\text{O}_2 = \frac{2x}{11.2} = \frac{x}{5.6} \text{ N}$$

Redox titrations (excluding iodometric and iodimetric) are summarised in Table 7.6

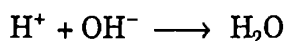
Table 7.6 Redox Titrations (Excluding Iodometric/Iodimetric)

| Estimation of                  | By titrating with            | Reactions                                                                                                                                                                               | Relation* between O.A. and R.A.                                                                                                              |
|--------------------------------|------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|
| 1. $\text{Fe}^{2+}$            | $\text{MnO}_4^-$             | $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-$ $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$                                        | $5\text{Fe}^{2+} \equiv \text{MnO}_4^-$ $\text{Eq. wt. } \text{Fe}^{2+} = M/1$ $\text{Eq. wt. } \text{MnO}_4^- = M/5$                        |
| 2. $\text{Fe}^{2+}$            | $\text{Cr}_2\text{O}_7^{2-}$ | $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-$ $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$                          | $6\text{Fe}^{2+} \equiv \text{Cr}_2\text{O}_7^{2-}$ $\text{Eq. wt. } \text{Cr}_2\text{O}_7^{2-} = M/6$                                       |
| 3. $\text{C}_2\text{O}_4^{2-}$ | $\text{MnO}_4^-$             | $\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{CO}_2 + 2e^-$ $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$                              | $5\text{C}_2\text{O}_4^{2-} \equiv 2\text{MnO}_4^-$ $\text{Eq. wt. } \text{C}_2\text{O}_4^{2-} = M/2$ $\text{Eq. wt. } \text{MnO}_4^- = M/5$ |
| 4. $\text{H}_2\text{O}_2$      | $\text{MnO}_4^-$             | $\text{H}_2\text{O}_2 \longrightarrow 2\text{H}^+ + \text{O}_2 + 2e^-$                                                                                                                  | $5\text{H}_2\text{O}_2 \equiv 2\text{MnO}_4^-$ $\text{Eq. wt. } \text{H}_2\text{O}_2 = M/2$ $\text{Eq. wt. } \text{MnO}_4^- = M/5$           |
| 5. $\text{As}_2\text{O}_3$     | $\text{MnO}_4^-$             | $\text{As}_2\text{O}_3 + 5\text{H}_2\text{O} \longrightarrow 2\text{AsO}_4^{3-} + 10\text{H}^+ + 4e^-$                                                                                  | $\text{Eq. wt. } \text{As}_2\text{O}_3 = M/4$                                                                                                |
| 6. $\text{AsO}_3^{3-}$         | $\text{BrO}_3^-$             | $\text{AsO}_3^{3-} + \text{H}_2\text{O} \longrightarrow \text{AsO}_4^{3-} + 2\text{H}^+ + 2e^-$ $\text{BrO}_3^- + 6\text{H}^+ + 6e^- \longrightarrow \text{Br}^- + 3\text{H}_2\text{O}$ | $\text{Eq. wt. of } \text{AsO}_3^{3-} = M/2$ $\text{Eq. wt. of } \text{BrO}_3^- = M/6$                                                       |

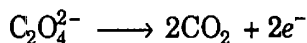
\*M is molar mass of O.A. or R.A.

**Illustration 1** A solution of  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  is 0.2N as an acid. What is its normality as reducing agent?

**Solution**  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \rightleftharpoons \text{K}^+ + 3\text{H}^+ + 2\text{C}_2\text{O}_4^{2-}$   
ion is neutralised by  $\text{OH}^-$



$\text{C}_2\text{O}_4^{2-}$  ion is oxidised hence, it is a reducing agent



Since, there are three ionisable  $\text{H}^+$  ions hence,

$$N_1 (\text{acid}), \text{normality} = M \times 3$$

and since there are two  $\text{C}_2\text{O}_4^{2-}$  ions exchanging four electrons, hence,

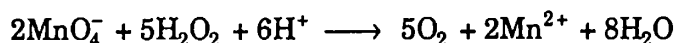
$$N_2 (\text{reducing agent}), \text{normality} = \text{molarity} (M) \times 4$$

$$\text{As an acid } 3M = 0.2 \text{ N (given)}$$

$$\therefore M = \frac{0.2}{3} = \frac{M}{15}$$

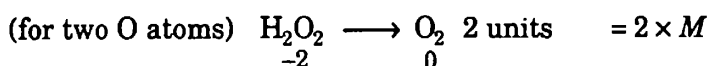
$$\therefore N_2 (\text{reducing agent}) = 4 \times \frac{1}{15} = \frac{4}{15} = 0.267 \text{ M}$$

**Illustration 2** The concentration of a hydrogen peroxide solution can be conveniently determined by titration against a standardised potassium permanganate solution in an acidic medium according to the following equation:



If 36.44 mL of 0.01652 M  $\text{KMnO}_4$  solution are required to completely oxidise 25 mL of a  $\text{H}_2\text{O}_2$  solution, calculate the molarity of the  $\text{H}_2\text{O}_2$  solution.

**Solution Method I**



Thus, 25.00 mL of

$$M_1 \text{H}_2\text{O}_2 \equiv 36.44 \text{ mL of } 0.01652 \text{ M } \text{MnO}_4^-$$

Using,

$$N_1 V_1 = N_2 V_2$$



$$25.00 \times 2M_1 \text{ H}_2\text{O}_2 = 36.44 \times 5 \times 0.01652 \text{ M MnO}_4^-$$

$$M_1 = \frac{36.44 \times 5 \times 0.01652}{25 \times 2}$$

$$= 0.0602 \text{ M}$$

**Method II** Number of moles of

$$\text{MnO}_4^- \text{ used} = \frac{36.44 \times 0.01652}{1000}$$

$$= 0.602 \times 10^{-3} \text{ mol}$$

$$\text{Number of moles of H}_2\text{O}_2 = 2.5 \times \text{mol of MnO}_4^-$$

$$= 1.505 \times 10^{-3} \text{ mol}$$

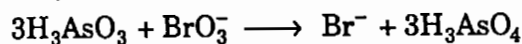
$$\text{Let molarity of H}_2\text{O}_2 = M_1$$

$$\text{then number of moles of H}_2\text{O}_2 = \frac{25 \times M_1}{1000}$$

$$\therefore \frac{25 \times M_1}{1000} = 1.505 \times 10^{-3}$$

$$\therefore M_1 = \frac{1.505 \times 10^{-3} \times 1000}{25} = 0.0602 \text{ M}$$

**Illustration 3**  $\text{KBrO}_3$  can be used to determine the concentration of As(III)



What is the molar concentration of As(III) in a solution if 22.35 mL of 0.10 M  $\text{KBrO}_3$  is needed to titrate 50.00 mL of As(III) solution?

**Solution** Let molar concentration of a solution containing As(III) =  $M_1$

|                                |                                  | Change in O.N.                 | Normality               |
|--------------------------------|----------------------------------|--------------------------------|-------------------------|
| $\text{H}_3\text{AsO}_3$<br>+3 | $\xrightarrow{\text{oxidation}}$ | $\text{H}_3\text{AsO}_4$<br>+5 | 2 units<br>2 × molarity |
| $\text{BrO}_3^-$<br>+5         | $\xrightarrow{\text{reduction}}$ | $\text{Br}^-$<br>-1            | 6 units<br>6 × molarity |

$$N_1 V_1 = N_2 V_2$$

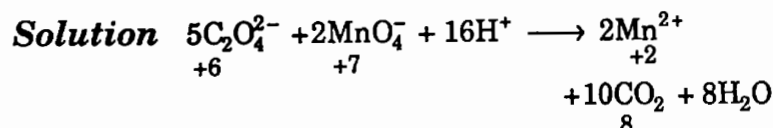
$$\text{As(III)} \quad \text{BrO}_3^-$$

$$2 \times M_1 \times 50 = 6 \times 0.10 \times 22.35$$

$$M_1 = \frac{6 \times 0.10 \times 22.35}{100}$$

$$= 0.1341 \text{ M}$$

**Illustration 4** Titration of 0.1467 g of primary standard  $\text{Na}_2\text{C}_2\text{O}_4$  required 28.85 mL of  $\text{KMnO}_4$  solution. Calculate the molar concentration of  $\text{KMnO}_4$  solution.



**Method I** (Based on number of equivalent)

In a reaction (redox/neutralisation) number of equivalents of different reactants are same.

$$\text{Equivalent of C}_2\text{O}_4^{2-} = \text{equivalents of MnO}_4^-$$

$$\text{Equivalent weight of C}_2\text{O}_4^{2-} = \frac{\text{molecular weight}}{2}$$

$$\therefore \text{Molarity} = 2 \times \text{normality}$$

$$\text{Equivalent weight of MnO}_4^- = \frac{\text{molecular weight}}{5}$$

$$\therefore \text{Molarity} = 5 \times \text{normality}$$

$$\text{Let molarity of MnO}_4^- = M_1$$

$$\text{normality} = 5M_1$$

$$\text{Number of equivalents of MnO}_4^- = \frac{28.85 \times 5M_1}{1000}$$

$$\text{Number of equivalents of Na}_2\text{C}_2\text{O}_4 = \frac{0.1467}{67}$$

$$\therefore \frac{28.85 \times 5M_1}{1000} = \frac{0.1467}{67}$$

$$\therefore M_1 = 0.01518 \text{ M}$$

**Method II** (Based on stoichiometric molar coefficients)

$$\text{Moles of MnO}_4^- = \frac{28.85M_1}{1000}$$

$$\text{Moles of Na}_2\text{C}_2\text{O}_4 = \frac{0.1467}{134}$$

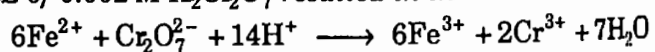
$$5 \text{ mol C}_2\text{O}_4^{2-} = 2 \text{ mol MnO}_4^-$$

$$\therefore \frac{0.1467}{134} \text{ mol C}_2\text{O}_4^{2-} = \frac{2}{5} \times \frac{0.1467}{134} \text{ mol MnO}_4^-$$

$$\therefore \frac{2}{5} \times \frac{0.1467}{134} = \frac{28.85M_1}{1000}$$

$$\therefore M_1 = 0.01518 \text{ M}$$

**Illustration 5** A 100 mL of sample of water was treated to convert any iron present to  $\text{Fe}^{2+}$ . Addition of 25 mL of 0.002 M  $\text{K}_2\text{Cr}_2\text{O}_7$  resulted in the reaction:



The excess  $\text{K}_2\text{Cr}_2\text{O}_7$  was back-titrated with 7.50 mL of 0.01 M  $\text{Fe}^{2+}$  solution. Calculate the parts per million of iron in the sample

**Solution** In the given reaction equivalents of  $\text{Cr}_2\text{O}_7^{2-}$  = equivalents of  $\text{Fe}^{2+}$

Unreacted  $\text{Cr}_2\text{O}_7^{2-}$  has been determined by titration with standard 0.01 M  $\text{Fe}^{2+}$  solution.

**Method 1** Let unreacted  $\text{Cr}_2\text{O}_7^{2-} = V \text{ mL}$

$$0.01 \text{ M Fe}^{2+} = 0.01 \text{ N Fe}^{2+}$$

$$0.002 \text{ M Cr}_2\text{O}_7^{2-} = 0.012 \text{ N Cr}_2\text{O}_7^{2-}$$

$$\therefore \begin{array}{ccc} N_1 V_1 & = & N_2 V_2 \\ \text{Cr}_2\text{O}_7^{2-} & & \text{Fe}^{2+} \end{array}$$

$$0.012 \times V = 0.01 \times 7.50$$

$$\therefore V (\text{unreacted Cr}_2\text{O}_7^{2-}) = \frac{0.01 \times 7.50}{0.012} = 6.25 \text{ mL}$$

$$\begin{aligned} \therefore \text{Volume of Cr}_2\text{O}_7^{2-} \text{ used by Fe}^{2+} (\text{in water sample}) &= 25.00 - 6.25 \\ &= 18.75 \text{ mL} \end{aligned}$$

$$\therefore \text{Equivalents of } \text{Cr}_2\text{O}_7^{2-} \text{ used} = \frac{18.75 \times 0.012}{1000} \\ = 2.25 \times 10^{-4}$$

$$\therefore \text{Equivalents of } \text{Fe}^{2+} \text{ in water} = 2.25 \times 10^{-4}$$

$$\text{Thus, Fe present in 100 mL water} = 2.25 \times 10^{-4} \times 56 \text{ g} \\ = 0.0126 \text{ g}$$

$$\text{Fe parts per million} = \frac{0.0126}{100} \times 10^6 \\ = 126 \text{ ppm}$$

$$\text{Method II Volume of } \text{Cr}_2\text{O}_7^{2-} \text{ used} = 18.75 \text{ mL}$$

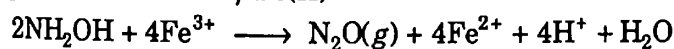
$$\text{Moles of } \text{Cr}_2\text{O}_7^{2-} \text{ used} = \frac{18.75 \times 0.002}{1000} \\ = 3.75 \times 10^{-5} \text{ mol}$$

$$\text{Moles of } \text{Fe}^{2+} \text{ (based on reaction)} = 6 \times \text{Cr}_2\text{O}_7^{2-} \\ = 6 \times 3.75 \times 10^{-5} \text{ mol}$$

$$\therefore \text{Fe present in 100 mL } \text{H}_2\text{O} = 2.25 \times 10^{-4} \text{ mol} \\ = 2.25 \times 10^{-4} \times 56 \text{ g} \\ = 0.0126 \text{ g}$$

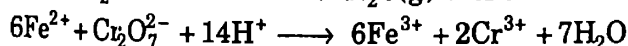
$$\text{Fe parts per million} = 126 \text{ ppm}$$

**Illustration 6** Treatment of hydroxylamine ( $\text{NH}_2\text{OH}$ ) with an excess of  $\text{Fe(III)}$  results in the formation of  $\text{N}_2\text{O}$  and an equivalent amount of  $\text{Fe(II)}$



Calculate the molar concentration of an  $\text{NH}_2\text{OH}$  solution if  $\text{Fe(II)}$  produced from 50 mL solution required 23.61 mL of 0.0217 M  $\text{K}_2\text{Cr}_2\text{O}_7$ .

**Solution**  $\text{Fe}^{2+}$  obtained by reduction of  $\text{Fe}^{3+}$  by  $\text{NH}_2\text{OH}$  is estimated by  $\text{Cr}_2\text{O}_7^{2-}$ .



Based on stoichiometric coefficients :

$$1 \text{ Cr}_2\text{O}_7^{2-} \equiv 6\text{Fe}^{2+} \equiv 3 \text{ NH}_2\text{OH}$$

$$\text{or } 1 \text{ mol Cr}_2\text{O}_7^{2-} \equiv 3 \text{ mol NH}_2\text{OH}$$

$$\therefore \frac{23.61 \times 0.0217}{1000} \text{ mol Cr}_2\text{O}_7^{2-}$$

$$= \frac{3 \times 23.61 \times 0.0217}{1000} \text{ mol NH}_2\text{OH}$$

$$= 1.537 \times 10^{-3} \text{ mol NH}_2\text{OH in 50 mL solution}$$

$$\therefore \text{Molar concentration of NH}_2\text{OH} = \frac{1.537 \times 10^{-3}}{0.050} \\ = 0.0307 \text{ M}$$

**Illustration 7** The  $\text{SO}_2$  present in air is mainly responsible for the acid-rain phenomenon. Its concentration can be determined by titration against a standard permanganate solution as follows :



Calculate the number of grams of  $\text{SO}_2$  in a sample of air if 7.37 mL of 0.008 M  $\text{KMnO}_4$  solution are required for the titration.

**Solution** Number of moles of  $\text{MnO}_4^-$  required

$$= \frac{7.37 \times 0.008}{1000} = 5.896 \times 10^{-5} \text{ mol}$$

Also, number of moles of

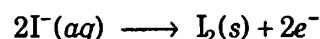
$$\text{SO}_2 = 2.5 \times \text{number of moles of } \text{MnO}_4^- \\ = 1.474 \times 10^{-4} \text{ mol}$$

$$\text{SO}_2 \text{ in air sample} = 1.474 \times 10^{-4} \times 64 \text{ g} \\ = 9.434 \times 10^{-3} \text{ g}$$

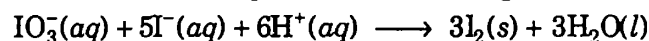
## Iodometric/Iodimetric Titrations

Compounds containing iodine are widely used in titrations.

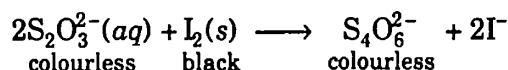
(i) Iodide ions can be oxidised to  $\text{I}_2$  by suitable oxidising agents



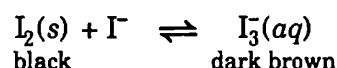
(ii) Iodate (V) ions,  $\text{IO}_3^-$ , will oxidise  $\text{I}^-$  to  $\text{I}_2$



(iii) Thiosulphate ions, ( $\text{S}_2\text{O}_3^{2-}$ ) can reduce iodine to iodide ions.



Although solid iodine is black (deep violet) and insoluble in water, it is converted into soluble triiodide ions ( $\text{I}_3^-$ )



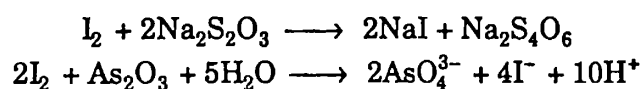
Small amount of iodine molecules ( $\text{I}_2$ ), gives blue colour with starch, hence, completion of the reaction can be detected when blue colour disappears at the end-point. It should be noted that starch, being colloidal, can adsorb  $\text{I}_2$  hence, it should be added when there is very small amount of  $\text{I}_2$  left (indicated by appearance of pale yellow colour) otherwise exact point is not detectable.

In all the titrations, KI is added to oxidising agent and  $\text{I}_2$  formed is estimated by sodium thiosulphate solution. These are summarised in Table 7.7.

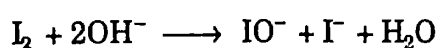
Table 7.7 Iodometric Titration (Titration Solution is  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ )

| S. No. | Estimation of,               | Reaction                                                                                                                                                                                                                                                                                                                                                                   | Relation between O.A. and R.A.                                                                                                                   |
|--------|------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------|
| 1.     | $\text{I}_2$<br>or           | $\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6^{2-}$ $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \longrightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$                                                                                                                                                       | $\text{I}_2 \equiv 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ $\text{Eq. wt. of Na}_2\text{S}_2\text{O}_3 = M/1$                         |
| 2.     | $\text{CuSO}_4$<br>or        | $2\text{CuSO}_4 + 4\text{KI} \longrightarrow \text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4 + \text{I}_2$ $\text{Cu}^{2+} + 4\text{I}^- \longrightarrow \text{Cu}_2\text{I}_2 + \text{I}_2$ <p style="text-align: center;">white ppt.</p>                                                                                                                                  | $2\text{CuSO}_4 \equiv \text{I}_2 \equiv 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ $\text{Eq. wt. of CuSO}_4 = M/1$                     |
| 3.     | $\text{CaOCl}_2$             | $\text{CaOCl}_2 + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + \text{Cl}_2$ $\text{Cl}_2 + 2\text{KI} \longrightarrow 2\text{KCl} + \text{I}_2$ $\text{Cl}_2 + 2\text{I}^- \longrightarrow 2\text{Cl}^- + \text{I}_2$                                                                                                                                              | $\text{CaOCl}_2 \equiv \text{Cl}_2 \equiv \text{I}_2 \equiv 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ $\text{Eq. wt. of CaOCl}_2 = M/2$ |
| 4.     | $\text{MnO}_2$<br>or         | $\text{MnO}_2 + 4\text{HCl}(\text{conc.}) \xrightarrow{\Delta} \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$ $\text{Cl}_2 + 2\text{KI} \longrightarrow 2\text{KCl} + \text{I}_2$ $\text{MnO}_2 + 4\text{H}^+ + 2\text{Cl}^- \longrightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} + \text{Cl}_2$ $\text{Cl}_2 + 2\text{I}^- \longrightarrow \text{I}_2 + 2\text{Cl}^-$ | $\text{MnO}_2 \equiv \text{Cl}_2 \equiv \text{I}_2 \equiv 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ $\text{Eq. wt. of MnO}_2 = M/2$     |
| 5.     | $\text{IO}_3^-$              | $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$                                                                                                                                                                                                                                                                              | $\text{IO}_3^- \equiv 3\text{I}_2 \equiv 6\text{I} \equiv 6\text{Na}_2\text{S}_2\text{O}_3$ $\text{Eq. wt. of IO}_3^- = M/6$                     |
| 6.     | $\text{H}_2\text{O}_2$       | $\text{H}_2\text{O}_2 + 2\text{I}^- + 2\text{H}^+ \longrightarrow \text{I}_2 + 2\text{H}_2\text{O}$                                                                                                                                                                                                                                                                        | $\text{H}_2\text{O}_2 \equiv \text{I}_2 \equiv 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ $\text{Eq. wt. of H}_2\text{O}_2 = M/2$        |
| 7.     | $\text{Cl}_2$                | $\text{Cl}_2 + 2\text{I}^- \longrightarrow 2\text{Cl}^- + \text{I}_2$                                                                                                                                                                                                                                                                                                      | $\text{Cl}_2 \equiv \text{I}_2 \equiv 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ $\text{Eq. wt. of Cl}_2 = M/2$                          |
| 8.     | $\text{O}_3$                 | $\text{O}_3 + 6\text{I}^- + 6\text{H}^+ \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$                                                                                                                                                                                                                                                                                 | $\text{O}_3 \equiv 3\text{I}_2 \equiv 6\text{I} \equiv 6\text{Na}_2\text{S}_2\text{O}_3$ $\text{Eq. wt. of O}_3 = M/6$                           |
| 9.     | $\text{ClO}^-$               | $\text{ClO}^- + 2\text{I}^- + 2\text{H}^+ \longrightarrow \text{H}_2\text{O} + \text{Cl}^- + \text{I}_2$                                                                                                                                                                                                                                                                   | $\text{ClO}^- \equiv \text{I}_2 \equiv 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ $\text{Eq. wt. of ClO}^- = M/2$                        |
| 10.    | $\text{Cr}_2\text{O}_7^{2-}$ | $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{I}^- \longrightarrow 3\text{I}_2 + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$                                                                                                                                                                                                                                              | $\text{Cr}_2\text{O}_7^{2-} \equiv 3\text{I}_2 \equiv 6\text{I}$ $\text{Eq. wt. of Cr}_2\text{O}_7^{2-} = M/6$                                   |
| 11.    | $\text{MnO}_4^-$             | $2\text{MnO}_4^- + 10\text{I}^- + 16\text{H}^+ \longrightarrow 2\text{MnO}_4^- + 5\text{I}_2 + 8\text{H}_2\text{O}$                                                                                                                                                                                                                                                        | $2\text{MnO}_4^- \equiv 5\text{I}_2 \equiv 10\text{I}$ $\text{Eq. wt. of MnO}_4^- = M/5$                                                         |
| 12.    | $\text{BrO}_3^-$             | $\text{BrO}_3^- + 6\text{I}^- + 6\text{H}^+ \longrightarrow \text{Br}^- + 3\text{I}_2 + 3\text{H}_2\text{O}$                                                                                                                                                                                                                                                               | $\text{BrO}_3^- \equiv 3\text{I}_2 \equiv 6\text{I}$ $\text{Eq. wt. of BrO}_3^- = M/6$                                                           |
| 13.    | As(V)                        | $\text{H}_3\text{AsO}_4 + 2\text{I}^- + 2\text{H}^+ \longrightarrow \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} + \text{I}_2$                                                                                                                                                                                                                                              | $\text{H}_3\text{AsO}_4 \equiv \text{I}_2 \equiv 2\text{I}$ $\text{Eq. wt. of H}_3\text{AsO}_4 = M/2$                                            |
| 14.    | $\text{HNO}_2$               | $2\text{HNO}_2 + 2\text{I}^- \longrightarrow \text{I}_2 + 2\text{NO} + \text{H}_2\text{O}$                                                                                                                                                                                                                                                                                 | $2\text{HNO}_2 \equiv \text{I}_2 \equiv 2\text{I}$ $\text{Eq. wt. of HNO}_2 = M/1$                                                               |
| 15.    | $\text{HClO}$                | $\text{HClO} + 2\text{I}^- + \text{H}^+ \longrightarrow \text{Cl}^- + \text{I}_2 + \text{H}_2\text{O}$                                                                                                                                                                                                                                                                     | $\text{Eq. wt. of HClO} = M/2$                                                                                                                   |

In **iodimetric** (different from iodometric) titration,  $\text{I}_2$  solution is taken in burette and reducing agents like sodium thiosulphate ( $\text{As}_2\text{O}_3$ ) etc. are taken in flask.

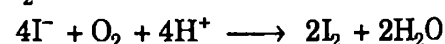


These titrations are usually performed in neutral or mildly alkaline (pH 8) to weakly acid solutions. If the pH is too alkaline,  $\text{I}_2$  will disproportionate to hypoiodate and iodide ions.



Weakly acidic medium is preferred since

- Starch used for the end-point detection tends to hydrolyse or decompose in strong acid.
- Reducing power of several reducing agents is increased in neutral solution.
- $\text{I}^-$  produced in the reaction tends to be oxidised by dissolved  $\text{O}_2$  in acid solution:

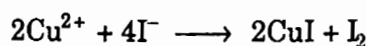


The pH for the titration of arsenic (III) with  $\text{I}_2$  can be maintained neutral by adding  $\text{NaHCO}_3$ . Iodimetric titrations have been summarised in Table 7.8.

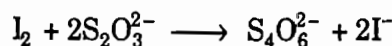
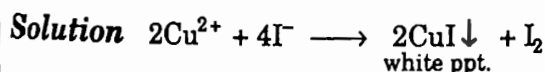
Table 7.8 Iodimetric Titration (Titrating Solution is  $I_2$  in KI)

| S. No. | Estimation                        | Reaction                                                            | Relation between O.A. and R.A.                                     |
|--------|-----------------------------------|---------------------------------------------------------------------|--------------------------------------------------------------------|
| 1.     | $H_2S$<br>(in acidic medium)      | $H_2S + I_2 \longrightarrow S + 2I^- + 2H^+$                        | $H_2S \equiv I_2 \equiv 2I$<br>Eq. wt. of $H_2S = M/2$             |
| 2.     | $SO_3^{2-}$<br>(in acidic medium) | $SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2I^- + 2H^+$    | $SO_3^{2-} \equiv I_2 \equiv 2I$<br>Eq. wt. of $SO_3^{2-} = M/2$   |
| 3.     | $Sn^{2+}$<br>(in acidic medium)   | $Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$                      | $Sn^{2+} \equiv I_2 \equiv 2I$<br>Eq. wt. of $Sn^{2+} = M/2$       |
| 4.     | As (III) (at pH 8)                | $H_2AsO_3^- + I_2 + H_2O \longrightarrow HAsO_4^{2-} + 2I^- + 3H^+$ | $H_2AsO_3^- \equiv I_2 \equiv 2I$<br>Eq. wt. of $H_2AsO_3^- = M/2$ |
| 5.     | $N_2H_4$                          | $N_2H_4 + 2I_2 \longrightarrow N_2 + 4H^+ + 4I^-$                   | $N_2H_4 \equiv 2I_2 \equiv 4I$<br>Eq. wt. of $N_2H_4 = M/4$        |

**Illustration 1** A 0.200 g sample containing copper is analysed iodometrically. Copper (II) is reduced to copper (I) by iodide.



What is the per cent copper in the sample if 20.0 mL of 0.10 M  $Na_2S_2O_3$  is required for titration of the liberated  $I_2$ ? ( $Cu = 63.5 \text{ g mol}^{-1}$ )



By stoichiometric coefficients:

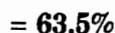
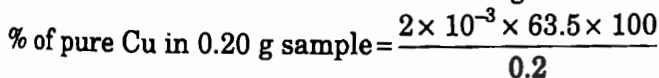
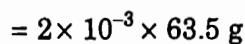
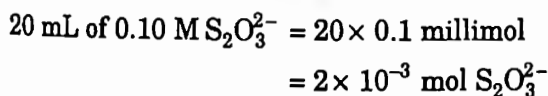
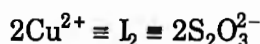
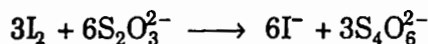
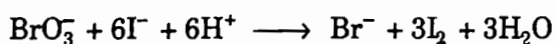
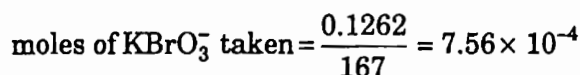
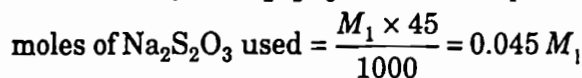


**Illustration 2** A solution of  $Na_2S_2O_3$  is standardised iodometrically against a 0.1262 g of pure  $KBrO_3$ , requiring 45.0 mL  $Na_2S_2O_3$  solution. What is the molarity of  $Na_2S_2O_3$  solution? ( $KBrO_3 = 167 \text{ g mol}^{-1}$ )

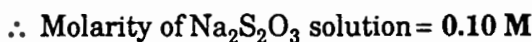
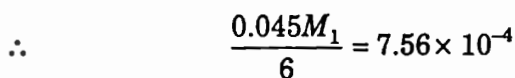
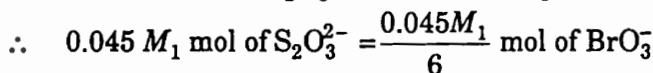
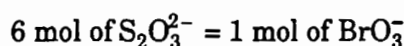
**Solution** The reactions are



Let, molarity of  $Na_2S_2O_3$  solution =  $M_1$



Based on stoichiometric coefficients:



## Target Practice 2

1. 100 mL of  $NaHC_2O_4$  (A) is neutralised by 100 mL of 1 M NaOH. Thus 100 mL of A will be oxidised by ..... mL of 1 M  $KMnO_4$  in acidic medium.

2.  $KMnO_4$  is reduced to  $MnCl_2$  in HCl medium, to  $MnO_2$  in KOH medium and to  $K_2MnO_4$  in  $H_2O$  medium.

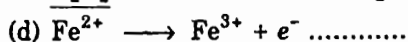
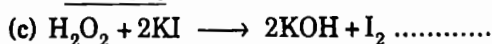
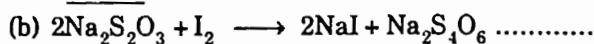
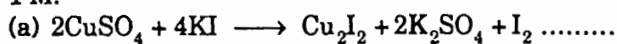
Thus, (a) in 1 M  $KMnO_4$  = ..... N in HCl medium

(b) 1 M  $KMnO_4$  = ..... N in KOH medium

(c) 1 M  $KMnO_4$  = ..... N in  $H_2O$  medium

3. We have 100 mL of 1 M  $KMnO_4$ . In acidic medium it is to be used. Calculate volume of water to be added so that it is 0.5 N. ....

4. Calculate normality of the underlined if each reactant is 1 M.

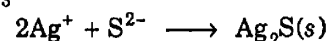


5. 10 mL of 1 M  $\text{Fe}^{2+}$  is oxidised by each of 1 M  $\text{MnO}_4^-$  and 1 M  $\text{Cr}_2\text{O}_7^{2-}$  in separate titration in acidic medium.  
Thus, volume of  $\text{MnO}_4^-$  required = ..... mL  
Volume of  $\text{Cr}_2\text{O}_7^{2-}$  required = ..... mL
6. 0.1 M HCl solution is being titrated by two students using 0.1 M NaOH.  
Student A: 20 mL of 0.1 M HCl + 40 mL  $\text{H}_2\text{O}$   
Student B: 20 mL of 0.1 M HCl + 80 mL of  $\text{H}_2\text{O}$ .

Calculate volume of NaOH in both cases.

- (a) .....  
(b) .....

7. A 100 mL sample of brackish water was made ammoniacal and sulphide it contained was titrated with 16.0 mL of 0.025 M  $\text{AgNO}_3$  solution.



Calculate concentration of  $\text{H}_2\text{S}$  in water in ppm. ....

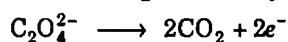
## Answers

1. 100 mL of  $\text{NaHC}_2\text{O}_4$  is neutralised by 100 mL of 1 M NaOH. This is an acid-base titration.  $\text{NaHC}_2\text{O}_4$  has one ionisable  $\text{H}^+$  ion, hence,

$$100 \times M_1 (= N_1) = 100 \times 1 \text{ M NaOH}$$

$$\therefore M_1 = N_1 (\text{NaHC}_2\text{O}_4) = 1$$

$\text{NaHC}_2\text{O}_4$  is oxidised to  $\text{CO}_2$  by  $\text{KMnO}_4$  in acidic medium.



Thus, 1 M  $\text{NaHC}_2\text{O}_4$  = 1 N as acid

= 2 N as reducing agent

1 M  $\text{KMnO}_4$  = 5 N as oxidising agent

$$\therefore 100 \times 2 \text{ N (A)} = V \times 5 \text{ N } \text{KMnO}_4$$

$$\therefore V = 40 \text{ mL}$$

2. (a) 5 N (b) 3 N (c) 1 N

3. 1 M  $\text{KMnO}_4$  = 5 N in acidic medium

$$100 \times 5 \text{ N} = V \times 0.5 \text{ N}$$

$$V = 1000 \text{ mL}$$

Thus, water to be added = 900 mL

4. (a)  $2\text{CuSO}_4 \equiv \text{I}_2 \equiv 2\text{I}$ ,

$$\text{CuSO}_4 \equiv \text{I} \therefore 1 \text{ M} = 1 \text{ N}$$

- (b)  $2\text{Na}_2\text{S}_2\text{O}_3 \equiv \text{I}_2 \equiv 2\text{I}$

$$\therefore \text{Na}_2\text{S}_2\text{O}_3 \equiv \text{I} \therefore 1 \text{ M} = 1 \text{ N}$$

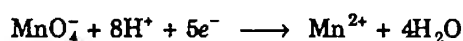
- (c)  $\text{H}_2\text{O}_2 \equiv \text{I}_2 \equiv 2\text{I}$

$$\therefore \text{I} = \frac{\text{H}_2\text{O}_2}{2} \therefore 1 \text{ M} = 2 \text{ N}$$

- (d)  $\text{Fe}^{2+} \equiv 1 e^-$

$$\therefore 1 \text{ M} = 1 \text{ N}$$

5.  $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-$

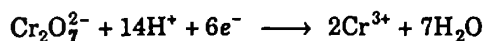


10 mL of 1 M  $\text{Fe}^{2+} \equiv 10 \text{ mL of } 1 \text{ N } \text{Fe}^{2+}$

V mL of 1 M  $\text{MnO}_4^- \equiv V \text{ mL of } 5 \text{ N } \text{MnO}_4^-$  in acidic medium

$$\therefore V \times 5 \text{ N} = 10 \times 1 \text{ N}$$

$$V = 2 \text{ mL}$$



V mL of 1 M  $\text{Cr}_2\text{O}_7^{2-} \equiv V \text{ mL of } 6 \text{ N } \text{Cr}_2\text{O}_7^{2-}$

$$\therefore V \times 6 \text{ N} = 10 \times 1 \text{ N}$$

$$\therefore V = \frac{10}{6} = 1.67 \text{ mL}$$

6. In both case same volume of NaOH is used.

$$(A) N_{\text{HCl}} (\text{resultant}) = \frac{20 \times 0.1}{60} = \frac{N}{30}$$

$$(B) N_{\text{HCl}} (\text{resultant}) = \frac{20 \times 0.1}{100} = \frac{N}{50}$$

Thus, resultant volume in A = 60 mL

$$60 \text{ mL of } \frac{N}{30} \equiv V \text{ mL of } 0.1 \text{ N NaOH}$$

$$\therefore V = 20 \text{ mL}$$

Resultant volume of B = 100 mL

$$100 \text{ mL of } \frac{N}{50} \equiv V \text{ mL of } 0.1 \text{ N NaOH}$$

$$\therefore V = 20 \text{ mL}$$

7. 16.0 mL of 0.025 M  $\text{AgNO}_3 \equiv 100 \text{ mL of } \text{H}_2\text{O}$  containing  $\text{H}_2\text{S}$

$$\text{Moles of } \text{AgNO}_3 = \frac{16 \times 0.025}{1000}$$

$$= 4 \times 10^{-4} \text{ mol}$$

$$\therefore \text{Moles of } \text{H}_2\text{S} = \frac{1}{2} \text{ mol of } \text{AgNO}_3$$

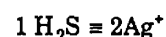
$$= 2 \times 10^{-4} \text{ mol } \text{H}_2\text{S}$$

$$= 2 \times 10^{-4} \times 34 \text{ g in } 100 \text{ mL } \text{H}_2\text{O}$$

$$= \frac{68 \times 10^{-4} \times 10^6}{100} \text{ g in } 10^6 \text{ mL (ppm) } \text{H}_2\text{O}$$

$$= 68 \text{ ppm}$$

Alternatively :



Thus, Normality of  $\text{H}_2\text{S} = 2 \times \text{Molarity}$

$$100 \times 2 \times M (\text{H}_2\text{S}) = 16.0 \times 0.025$$

$$M (\text{H}_2\text{S}) = 2 \times 10^{-3} \text{ mol L}^{-1}$$

$$= 68 \times 10^{-3} \text{ g L}^{-1}$$

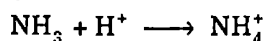
$$= 68 \times 10^{-3} \text{ g mL}^{-1}$$

$$= 68 \times 10^{-3} \times 10^3 \text{ g ppm}$$

$$= 68 \text{ ppm}$$

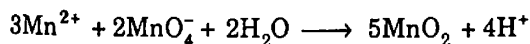
## Practice Exercise 2

1. Household ammonia, used as a window cleaner and for other cleaning purposes, is  $\text{NH}_3(aq)$ . 31.08 mL of 0.9928 M  $\text{HCl}(aq)$  is required to neutralise the  $\text{NH}_3$  present in a 5.00 mL sample,



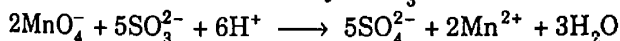
What is the molarity of  $\text{NH}_3$  in the sample?

2. What volume of a 0.232 N  $\text{HCl}$  solution contains  
(a) 3.17 meq. of solute  
(b) 6.5 eq. of solute?
3. Calculate the normality of each of the following solution:  
(a) 7.88 g of  $\text{HNO}_3$  per litre solution  
(b) 26.5 g of  $\text{Na}_2\text{CO}_3$  per litre solution (if acidified to form  $\text{CO}_2$ ).
4. How many (a) meq. (b) equivalent, (c) mole and (d) gram are present in 60 mL of 4.0 N  $\text{H}_2\text{SO}_4$ ?
5. What is the purity of conc.  $\text{H}_2\text{SO}_4$  ( $d = 1.8 \text{ g/mL}$ ) if 5.00 mL is neutralised by 84.6 mL of 2.00 N  $\text{NaOH}$ ?
6. Urea sample is 60% pure. Calculate volume of 1 N  $\text{HCl}$  required to absorb  $\text{NH}_3$  from 1.0 g of urea sample on decomposition with  $\text{NaOH}$ .
7.  $\text{Mn}^{2+}(aq)$  can be determined by titration with  $\text{KMnO}_4(aq)$

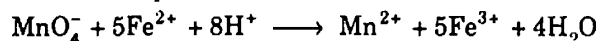


A 25.00 mL sample of  $\text{Mn}^{2+}(aq)$  requires 35 mL of 0.06 M  $\text{KMnO}_4(aq)$  for its titration. What is the molarity of the  $\text{Mn}^{2+}(aq)$ ?

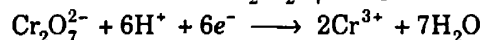
8. A particular acid-rain water has  $\text{SO}_3^{2-}$ . If a 25.00 mL sample of this water requires 34.08 mL of 0.01964 M  $\text{KMnO}_4$  for its titration, what is the molarity of  $\text{SO}_3^{2-}$  in acid-rain?



9. What is molarity of a  $\text{MnO}_4^-$  solution if 32.00 mL of the solution is required to titrate 40.00 mL of 0.400 N  $\text{Fe}^{2+}$ ?



10. In a reaction,  $\text{Cr}_2\text{O}_7^{2-}$  is reduced to  $\text{Cr}^{3+}$ . What is concentration of 0.1 M  $\text{K}_2\text{Cr}_2\text{O}_7$  in equivalent per litre?



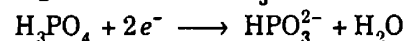
(Here we have given half reaction; if not given be careful in balancing affected atoms and in taking oxidation number of two Cr atoms)

11. What mass of phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is required to make 550 mL of 0.400 N solution?

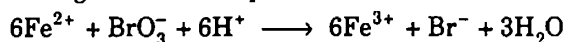
(a) assuming complete neutralisation of the acid



(b) assuming reduction to  $\text{HPO}_3^{2-}$ .



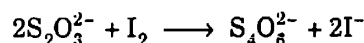
12. The concentration of  $\text{Fe}^{2+}$  ion in aqueous solution can be determined by redox titration with bromate ion,  $\text{BrO}_3^-$ , according to net ionic equation:



What is the molar concentration of  $\text{Fe}^{2+}$  if 31.50 mL of 0.10 M  $\text{KBrO}_3$  is required for complete reaction with 10.0 mL of the  $\text{Fe}^{2+}$  solution?

13. A 1.100 g sample of copper ore is dissolved and the  $\text{Cu}^{2+}(aq)$  is treated with excess  $\text{KI}$ . The liberated  $\text{I}_2$  requires 12.12 mL of 0.10 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution for titration. What is % copper by mass in the ore?

14. What mass of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  is needed to make 500 mL of 0.200 N solution for the reaction?



## Answers

1.  $M(\text{NH}_3) \times 5 = 0.9928 \times 31.08 \text{ HCl}$

$$M(\text{NH}_3) = 6.17 \text{ M}$$

2. (a)  $N \times V \text{ (mL)} = \text{milliequiv.}$

$$0.232 \times V = 3.17$$

$$\therefore V = \frac{3.17}{0.232} = 13.66 \text{ mL}$$

$$(b) \frac{N \times V \text{ (mL)}}{1000} = \text{equiv.}$$

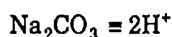
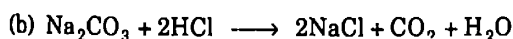
$$\frac{0.232 \times V}{1000} = 6.5$$

$$V = 2.8017 \times 10^4 \text{ mL} = 28.017 \text{ L}$$

3. (a)  $7.88 \text{ g L}^{-1} \text{ HNO}_3 = \frac{7.88}{63} \text{ mol L}^{-1}$

$$= 0.125 \text{ M}$$

$$= 0.125 \text{ N (being monobasic acid)}$$



$$\therefore \text{Normality of Na}_2\text{CO}_3 = 2 \times \text{molarity}$$

$$26.5 \text{ Na}_2\text{CO}_3 \text{ per litre} = \frac{26.5}{106} \text{ mol L}^{-1} = 0.25 \text{ M}$$

$$\therefore \text{Normality} = 0.50 \text{ N}$$

4. (a)  $\text{meq} = \text{normality} \times \text{volume (mL)}$

$$= 4.0 \times 60$$

$$= 240$$

$$(b) \text{eq} = 0.240$$

$$(c) \text{mol} = \frac{0.240}{2} = 0.120 \text{ mol}$$

$$(d) \text{gram} = 0.120 \times 98 = 11.76 \text{ g}$$

5. 5.00 mL of  $\text{H}_2\text{SO}_4 = 84.6 \text{ mL}$  of 2.00 N  $\text{NaOH}$

$$\therefore N(\text{H}_2\text{SO}_4) = 33.84 \text{ N}$$

$$\therefore M(\text{H}_2\text{SO}_4) = 16.92 \text{ M}$$

$$1000 \text{ mL H}_2\text{SO}_4 \text{ has} = 16.92 \text{ mol H}_2\text{SO}_4$$

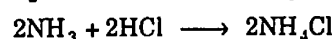
since, mass/volume = density

$$\therefore 1000 \times 1.8 \text{ g H}_2\text{SO}_4 \text{ has} = 16.92 \times 98 \text{ g H}_2\text{SO}_4$$

$$\therefore 100 \text{ g H}_2\text{SO}_4 \text{ has} = \frac{16.92 \times 98 \times 100}{1000 \times 1.8}$$

$$= 92.12\%$$

6.  $\text{NH}_2\text{CONH}_2 + 2\text{NaOH} \longrightarrow 2\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}$

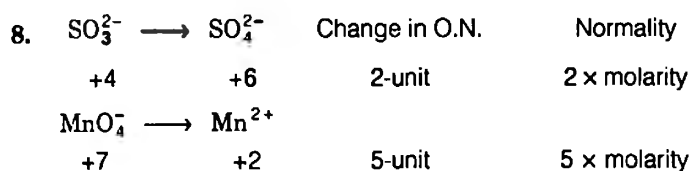
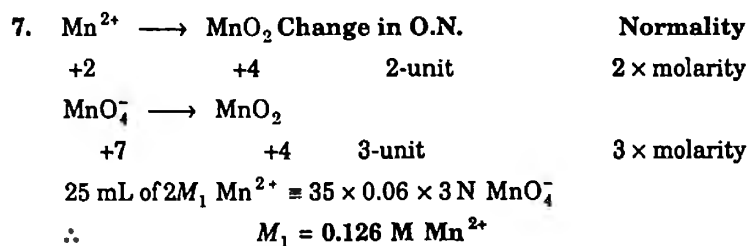


$$1.0 \text{ g impure } \text{NH}_2\text{CONH}_2 = 0.6 \text{ g pure } \text{NH}_2\text{CONH}_2 \\ = 0.01 \text{ mol}$$

$$\therefore \text{HCl required by } 0.01 \text{ mol urea} = 0.02 \text{ mol} \\ = 20 \text{ millimol}$$

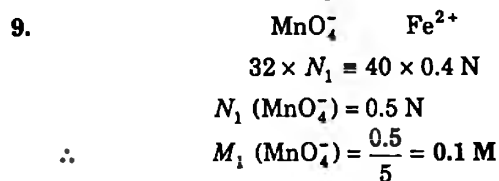
$$1 \times V = 20$$

$$\therefore V = 20 \text{ mL}$$



$$25 \times 2M_1 (\text{SO}_3^{2-}) \text{ in } \text{H}_2\text{O} \equiv 34.08 \times 0.01964 \times 5 \text{ MnO}_4^-$$

$$\therefore M_1 = 0.0669 \text{ M SO}_3^{2-}$$



10.  $0.1 \text{ M K}_2\text{Cr}_2\text{O}_7 \equiv 0.6 \text{ N K}_2\text{Cr}_2\text{O}_7$

11. (a) All the  $\text{H}^+$  ions are neutralised.

$$\text{Thus, } 0.400 \text{ N} = \frac{0.400}{3} \text{ M H}_3\text{PO}_4$$

$$\text{Thus, moles of H}_3\text{PO}_4 \text{ in } 550 \text{ mL} = \frac{0.400 \times 550}{3 \times 1000}$$

$$\therefore \text{Mass of H}_3\text{PO}_4 = 0.073 \text{ mol} \\ = 7.1867 \text{ g}$$

(b) It is reduced to  $\text{HPO}_3^{2-}$

$$\therefore 1 \text{ H}_3\text{PO}_4 \equiv 2e^-$$

$$\therefore 1 e^- \equiv \frac{\text{H}_3\text{PO}_4}{2}$$

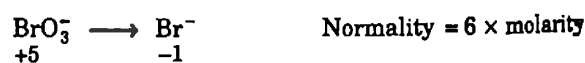
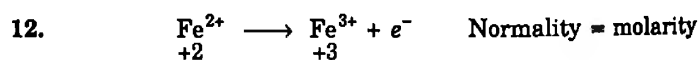
$$\therefore 0.400 \text{ N} = \frac{0.400}{2} \text{ M H}_3\text{PO}_4$$

Thus, moles of  $\text{H}_3\text{PO}_4$  in 550 mL

$$= \frac{0.400 \times 550}{2 \times 1000} \text{ mol}$$

$$= 0.11 \text{ mol}$$

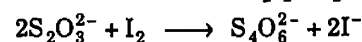
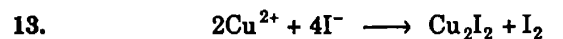
$$= 10.78 \text{ g}$$



$$10.00 \times N_1 \equiv 31.50 \times 0.10 \times 6 \text{ N BrO}_3^-$$

$$\therefore N_1 (\text{Fe}^{2+}) = 1.89 \text{ N}$$

$$= 1.89 \text{ M Fe}^{2+}$$



$$2\text{Cu}^{2+} \equiv \text{I}_2 \equiv 2\text{I}$$

$$\therefore 1 \text{ Cu}^{2+} \equiv \text{I} \equiv \text{S}_2\text{O}_3^{2-}$$

$$\therefore 1 \text{ mol Cu}^{2+} = 1 \text{ equivalent Cu}^{2+}$$

Also,  $2\text{S}_2\text{O}_3^{2-} \equiv \text{I}_2 \equiv 2\text{I}$

$$\therefore 1 \text{ S}_2\text{O}_3^{2-} \equiv \text{I}$$

$$\therefore 1 \text{ mol S}_2\text{O}_3^{2-} \equiv 1 \text{ equivalent S}_2\text{O}_3^{2-} \equiv \text{Cu}^{2+}$$

$$\text{Moles of Cu}^{2+} \equiv \text{moles of S}_2\text{O}_3^{2-}$$

$$= \frac{12.12 \times 0.1}{1000}$$

$$= 1.212 \times 10^{-3} \text{ mol}$$

$$= 1.212 \times 10^{-3} \times 63.5 \text{ g}$$

$$= 0.076962 \text{ g}$$

It is present in 1.1 g impure Cu ore

$$\% \text{ of Cu}^{2+} \text{ in sample} = \frac{0.076962}{1.100} \times 100$$

$$= 6.996\%$$

14. As in Q. 13

$$500 \text{ mL of } 0.200 \text{ N Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$$

$$\equiv 500 \times 0.200 \text{ millimol}$$

$$= 0.1 \text{ mol}$$

$$= 24.8 \text{ g Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$$

# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** What are the molar concentrations of the solutes listed below **when** dissolved in water?

- (a) 3.28 mol  $C_2H_5OH$  in 7.16 L of solution
- (b)  $3.67 \times 10^{-3}$  mol  $CH_3OH$  in 50.00 mL of solution
- (c) 22.3 g  $(CH_3)_2CO$  in 125 mL solution
- (d) 14.5 mL of pure glycerol;  $C_3H_8O_3$  ( $d = 1.26 \text{ g/cm}^3$ ) in 425 mL solution

$$\begin{aligned} \text{Plan } \text{Molarity} &= \text{mol L}^{-1} = \frac{\text{g}}{\text{g mol}^{-1} \times \text{L}} \\ &= \frac{\text{g} \times 1000}{\text{g mol}^{-1} \times \text{mL}} \\ \text{mass} &= \text{volume} \times \text{density} \end{aligned}$$

**Solution** (a) 3.28 mol  $C_2H_5OH$  is 7.16 L of solution

$$\therefore M(C_2H_5OH) = \frac{3.28}{7.16} \text{ mol L}^{-1} = 0.458 \text{ M}$$

(b)  $3.67 \times 10^{-3}$  mol  $CH_3OH$  in 50.00 mL (= 0.05 L) solution

$$\therefore M(CH_3OH) = \frac{3.67 \times 10^{-3}}{0.05} \text{ mol L}^{-1} = 0.0734 \text{ M}$$

(c) 22.3 g  $(CH_3)_2CO$  in 125 mL solution

$$= \frac{22.3}{58} \text{ mol } (CH_3)_2CO \text{ in } 0.125 \text{ L solution}$$

$$\therefore M[(CH_3)_2CO] = \frac{22.3}{0.125 \times 58} \text{ mol L}^{-1} = 3.076 \text{ M}$$

(d) 14.5 mL of pure glycerol =  $14.5 \times 1.26 \text{ g}$

$$= \frac{14.5 \times 1.26}{92} \text{ mol in } 0.425 \text{ L solution}$$

$$\therefore M(\text{glycerol}) = 0.467 \text{ M}$$

**Problem 2.** Water is evaporated from 135 mL of 0.224 M  $MgSO_4$  solution until the solution volume becomes 105 mL. What is the molarity of  $MgSO_4$  in the solution that results?

**Plan** When solution is evaporated, volatile solvent (like  $H_2O$ ) evaporates, but non-volatile solute remains unaffected. Due to change in volume of solution, molarity also changes.

**Solution** 135 mL of 0.224 M  $MgSO_4$  solution  
 $= 135 \times 0.224$  millimol of  $MgSO_4$

$$= \frac{135 \times 0.224}{1000} \text{ mol } MgSO_4$$

$$= 0.0302 \text{ mol } MgSO_4$$

Same amount is present in 105 mL solution after evaporation of water.

Thus, 105 mL solution has = 0.0302 mol  $MgSO_4$

$$1000 \text{ mL solution has} = \frac{0.0302}{105} \times 1000 = 0.288 \text{ M}$$

**Alternate method**  $M_1 V_1 = M_2 V_2$   
 initial final

$$0.224 \times 135 = M_2 \times 105$$

$$M_2 = 0.228 \text{ M}$$

**Problem 3.** Find the volume of a 0.2 M solution of  $MnO_4^-$  which will react with 50.0 mL of 0.1 M solution of  $C_2O_4^{2-}$  in acidic medium.

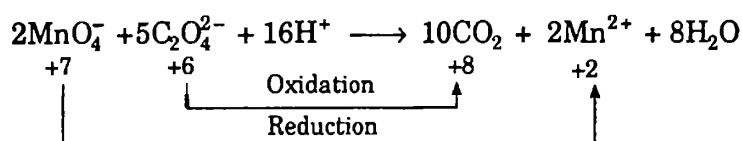
**Plan** Normality of  $MnO_4^- = 5 \times \text{molarity}$

and normality of  $C_2O_4^{2-} = 2 \times \text{molarity}$

use  $N_1 V_1 = N_2 V_2$

Milliequivalents of reacting species are equal.

**Solution**



**Note:** We have taken oxidation number of two C atoms in  $C_2O_4^{2-}$  (true definition of O.N.) hence, we also take O.N. of two C atoms in  $CO_2$ .

Thus,  $N(MnO_4^-) = \text{change in O.N.} \times M$

$$N = 5 \times 0.2 = 1 \text{ N}$$

$$N(C_2O_4^{2-}) = 2 \times M = 2 \times 0.1 = 0.2 \text{ N}$$

using  $N_1 V_1(MnO_4^-) = N_2 V_2(C_2O_4^{2-})$

$$1.0 \times V_1 = 0.2 \times 50$$

$$V_1 = 10 \text{ mL } 0.2 \text{ M } MnO_4^-$$

**Note:** We can't use  $M_1 V_1 = M_2 V_2$  when change in O.N. or acidity and basicity are different.

**Alternate method** Let volume of  $MnO_4^- = V \text{ mL}$

$$V \text{ mL of } 0.2 \text{ M } MnO_4^- = 0.2 V \text{ millimol of } MnO_4^-$$

$$50 \text{ mL of } 0.1 \text{ M } C_2O_4^{2-} = 50 \times 0.1 = 5 \text{ millimol of } C_2O_4^{2-}$$

Using reaction: 5 mol of  $C_2O_4^{2-}$  are oxidised by

$$= 2 \text{ mol of } MnO_4^-$$



5 millimol of  $\text{C}_2\text{O}_4^{2-}$  are oxidised by = 2 millimol of  $\text{MnO}_4^-$   
 $0.2 \text{ V} = 2$   
 $\text{V} = 10 \text{ mL}$

**Problem 4.** Two acids, A and B are titrated separately. 25 mL of 1 N  $\text{Na}_2\text{CO}_3$  solution requires 10 mL of A and 40 mL of B for complete neutralisation. What volume of A and B would you mix to produce 1 L of 1 N acid solution?

**Plan** Normality of each acid is known by titration. Thus, from total normality and the relation

$$N_{\text{Total}} = \frac{\sum NV}{\sum V}$$

volume of each acid is determined.

**Solution** 10 mL of  $N_A$  acid A = 25 mL of 1 N  $\text{Na}_2\text{CO}_3$

$$N_A = 2.5$$

40 mL of  $N_B$  acid B = 25 mL of 1 N  $\text{Na}_2\text{CO}_3$

$$N_B = 0.625$$

Let volume of acid A =  $x \text{ L}$

and that of acid B =  $(1 - x) \text{ L}$

Resultant normality of mixture = 1 N

using relation  $N_{\text{mix}} = \frac{\sum NV}{\sum V} = \frac{N_A V_A + N_B V_B}{V_A + V_B}$

$$1 = \frac{2.5x + 0.625(1 - x)}{1}$$

$$x = 0.2 \text{ L}$$

Volume of acid A = 0.2 L

Volume of acid B = 0.8 L

**Problem 5.** A sample supposed to be pure  $\text{CaCO}_3$  is used to standardise a solution of HCl. The substance really was a mixture of  $\text{MgCO}_3$  and  $\text{BaCO}_3$ , but the standardisation of HCl was accurate. Find the percentage of  $\text{BaCO}_3$  and  $\text{MgCO}_3$  in the mixture. (Ca = 40, Mg = 24, Ba = 137)

**Plan**  $\text{CaCO}_3$  and mixture of  $\text{MgCO}_3$  and  $\text{BaCO}_3$  give same result in the standardisation of HCl hence,

Equivalent of  $\text{CaCO}_3$  = equivalent of  $\text{MgCO}_3$  and  $\text{BaCO}_3$

Thus, by assuming a quantity of  $\text{CaCO}_3$  (which is also equal to mixture of  $\text{MgCO}_3$  and  $\text{BaCO}_3$ ), % of each can be determined.

**Solution** Equivalent of  $\text{CaCO}_3$  = equivalent of mixture

$$\text{CaCO}_3 \equiv (\text{MgCO}_3 + \text{BaCO}_3)$$

Let  $\text{CaCO}_3$  be 100 g, g-equivalent =  $\frac{100}{50} = 2$

Let  $\text{MgCO}_3 = x \text{ g}$

$\text{BaCO}_3 = (100 - x) \text{ g}$

g-equivalent of  $\text{MgCO}_3 = \frac{x}{42}$

$$\text{g-equivalent of BaCO}_3 = \frac{100 - x}{197/2} = \frac{100 - x}{98.5}$$

$$\frac{x}{42} + \frac{100 - x}{98.5} = 2$$

This gives

$$x = 72.11$$

$\therefore \text{MgCO}_3 = 72.11\%$

$\text{BaCO}_3 = 27.89\%$

**Problem 6.** Determine the equivalent weight in each of the following

- the reduction half-reaction for the disproportionation of  $\text{Br}_2$  in base,
- the oxidation half-reaction which yields bromate ion,
- the overall reaction.

**Plan** Equivalent weight =  $\frac{\text{formula weight}}{\text{change in oxidation number}}$

and in a disproportionation reaction =  $E_O + E_R$

where,  $E_O$  is the equivalent weight in oxidation half-reaction and  $E_R$  is the equivalent weight in reduction half-reaction.

**Solution** (a)  $2e^- + \text{Br}_2 \longrightarrow 2\text{Br}^-$

$$\begin{aligned} \text{Eq. wt.} &= \frac{\text{mol. wt. of Br}_2}{2} = \frac{160}{2} \\ &= 80 \text{ g equiv}^{-1} \end{aligned}$$

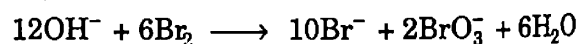
(b)  $\text{Br}_2 + 12\text{OH}^- \longrightarrow 2\text{BrO}_3^- + 6\text{H}_2\text{O} + 10e^-$

$$\text{Eq. wt.} = \frac{\text{mol. wt. of Br}_2}{10} = \frac{160}{10} = 16 \text{ g equiv}^{-1}$$

(c)  $6\text{OH}^- + 3\text{Br}_2 \longrightarrow 5\text{Br}^- + \text{BrO}_3^- + 3\text{H}_2\text{O}$

Since, number of electrons involved in each half-reaction should be identical, hence 10 electrons are involved in oxidation then 10 electrons should also be involved in reduction thus,

$$5 \times (a) + (b)$$



$$\text{Hence, Eq. wt. (Br}_2) = \frac{6 \times 160}{10} = 96.0 \text{ g equiv}^{-1}.$$

or net eq. wt. = eq. wt. of step (a) + eq. wt. of step (b) = 96

**Problem 7.** 100.0 mL sample of hard water is passed through a column of the ion exchange resin  $\text{H}_2\text{R}$ . The water coming off the column requires 15.17 mL of 0.0265 M NaOH for its titration. What is the hardness of the water expressed as ppm of  $\text{Ca}^{2+}$ ?

**Plan**  $\text{Ca}^{2+}$  in hard water replaces  $\text{H}^+$  of ion-exchange column



$$\text{mol of Ca}^{2+} = \frac{1}{2} \times \text{mol of OH}^-$$

Thus, ppm concentration of  $\text{Ca}^{2+}$  can be determined.



$$\begin{aligned}\text{Moles of CaSO}_4 &\equiv \text{moles of H}_2\text{SO}_4 = \frac{21.58 \times 10^{-3}}{1000} \\ &= 2.158 \times 10^{-5} \text{ mol}\end{aligned}$$

This amount is in 25 mL hard water

25 mL of hard water has hardness

$$\begin{aligned}&= 2.158 \times 10^{-5} \text{ mol CaSO}_4 \\ &= 2.158 \times 10^{-5} \times 136 \text{ g CaSO}_4\end{aligned}$$

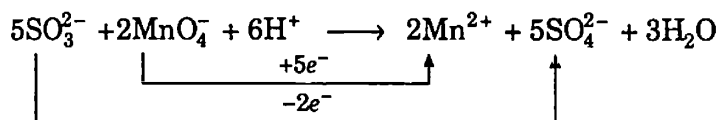
$10^6$  mL (per million) of hard water has hardness

$$\begin{aligned}&= \frac{2.158 \times 10^{-5} \times 136 \times 10^6}{25} \text{ g CaSO}_4 \\ &= 117.4 \text{ ppm CaSO}_4\end{aligned}$$

**Problem 11.** What mass of  $\text{Na}_2\text{SO}_3$  must have been present in a sample that required 26.50 mL of 0.0510 M  $\text{KMnO}_4$  for its oxidation to  $\text{Na}_2\text{SO}_4$  in acidic solution?

*Plan* Taking the fact that equivalent of  $\text{SO}_3^{2-} \equiv$  equivalent of  $\text{MnO}_4^-$  amount of  $\text{Na}_2\text{SO}_3$  can be calculated. or on comparison of moles of  $\text{MnO}_4^-$  and  $\text{SO}_3^{2-}$ , amount of  $\text{Na}_2\text{SO}_3$  can be calculated.

**Solution** Redox reaction is



$$\text{Equivalent weight of MnO}_4^- = \frac{M}{5}$$

$$\text{Equivalent weight of SO}_3^{2-} = \frac{M}{2}$$

26.50 mL of 0.0510 M  $\text{MnO}_4^-$

$$\begin{aligned}&\equiv 26.50 \text{ mL of } 0.2550 \text{ N MnO}_4^- \\ &\equiv 26.50 \text{ mL of } 0.2550 \text{ N SO}_3^{2-}\end{aligned}$$

$$\text{Equivalent of Na}_2\text{SO}_3 = \frac{0.2550 \times 26.50}{1000}$$

$$= 6.7575 \times 10^{-3}$$

$$\begin{aligned}\therefore \text{Weight of Na}_2\text{SO}_3 &= 6.75 \times 10^{-3} \times 63 \text{ g} \\ &= 0.426 \text{ g}\end{aligned}$$

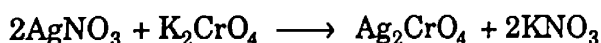
**Alternate method**

$$\text{Moles of MnO}_4^- = \frac{26.5 \times 0.051}{1000}$$

$$= 1.35 \times 10^{-3} \text{ mol}$$

$$\begin{aligned}\therefore \text{Moles of Na}_2\text{SO}_3 &= \frac{5}{2} \times 1.35 \times 10^{-3} \text{ mol} \\ &= 0.426 \text{ g}\end{aligned}$$

**Problem 12.** 25 mL of 0.1122 M  $\text{AgNO}_3$  is added to an excess of  $\text{K}_2\text{CrO}_4(aq)$ . What mass of  $\text{Ag}_2\text{CrO}_4$  will precipitate from the solution? (Ag = 108, Cr = 52, N = 14, O = 16)



$$\text{Plan } \frac{\text{Molarity} \times \text{volume in mL}}{1000} = \text{moles of the substance}$$

Based on reaction 2 mol  $\text{AgNO}_3 \equiv$  1 mol  $\text{Ag}_2\text{CrO}_4$

hence, number of moles of  $\text{Ag}_2\text{CrO}_4$  obtained from given mol of  $\text{AgNO}_3$  can be calculated.

**Solution** From the reaction:

2 mol of  $\text{AgNO}_3$  gives = 1 mol  $\text{Ag}_2\text{CrO}_4$

$$\text{hence, } \frac{25 \times 0.1122}{1000} \text{ mol of AgNO}_3 \text{ gives}$$

$$= \frac{25 \times 0.1122}{1000 \times 2} \text{ mol Ag}_2\text{CrO}_4$$

$$= 0.0014 \text{ mol Ag}_2\text{CrO}_4$$

$$= 0.0014 \times 332 \text{ g Ag}_2\text{CrO}_4$$

$$= 0.4656 \text{ g Ag}_2\text{CrO}_4$$

**Problem 13.** A sample of pure  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  requires 46.2 mL of 0.1 M  $\text{NaOH}$  for titration. How many millilitres of 0.1 M  $\text{KMnO}_4$  will the sample react?

*Plan*  $\text{NaOH}$  neutralises three ionisable  $\text{H}^+$  and each mole of the sample has two moles of  $\text{C}_2\text{O}_4^{2-}$  ions oxidised by  $\text{MnO}_4^-$ . Also

$$\text{moles of C}_2\text{O}_4^{2-} = \frac{2}{3} \text{ mol of H}^+$$

From the number of moles of  $\text{OH}^-$ , number of moles of  $\text{H}^+$  and hence that of  $\text{C}_2\text{O}_4^{2-}$  are known. Thus, volume of  $\text{MnO}_4^-$  required to oxidise  $\text{C}_2\text{O}_4^{2-}$  can be calculated.

**Solution**  $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O}$



Number of moles of  $\text{OH}^-$

$$\equiv \text{number of moles of H}^+ \text{ ion} = \frac{46.2 \times 0.1}{1000}$$

$$= 4.62 \times 10^{-3} \text{ mol}$$

$\therefore$  Number of moles of  $\text{C}_2\text{O}_4^{2-}$  ion

$$= \frac{2}{3} \times 4.62 \times 10^{-3} = 3.08 \times 10^{-3} \text{ mol}$$

Since, 5 mol of  $\text{C}_2\text{O}_4^{2-} \equiv$  2 mol of  $\text{MnO}_4^-$

$$\begin{aligned}\therefore 3.08 \times 10^{-3} \text{ mol of C}_2\text{O}_4^{2-} &= \frac{2}{5} \times 3.08 \times 10^{-3} \\ &= 1.232 \times 10^{-3} \text{ mol MnO}_4^-\end{aligned}$$

If V mL of 0.1 M  $\text{MnO}_4^-$  are required, then

$$\frac{V \times 0.1}{1000} = 1.232 \times 10^{-3}$$

$$\therefore V = 12.32 \text{ mL}$$

**Alternate method**

Sample has three  $\text{H}^+$  ions

$\therefore$  46.2 mL of 0.1 M  $\text{NaOH} \equiv 3\text{H}^+$  ions

$$\therefore \text{Equivalent of salt as acid} = \frac{46.2 \times 0.1}{3 \times 1000} = 1.54 \times 10^{-3}$$

$$\therefore \text{Equivalent of C}_2\text{O}_4^{2-} \text{ in two oxalates} = 6.16 \times 10^{-3}$$

$$\text{Equivalent of } 0.1 \text{ M MnO}_4^- = \frac{V \times 0.1 \times 5}{1000}$$

$$\therefore \frac{V \times 0.1 \times 5}{1000} = 6.16 \times 10^{-3}$$

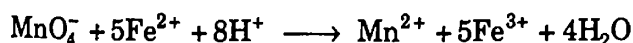
$$\therefore V = 12.32 \text{ mL}$$

**Problem 14.** A 0.8040 g sample of an iron ore is dissolved in acid. The iron is then reduced to  $\text{Fe}^{2+}$  and titrated with 47.22 mL of 0.02242 M  $\text{KMnO}_4$  solution.

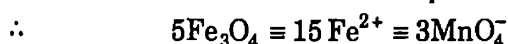
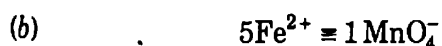
Calculate the results of this analysis in terms of

(a) % Fe ( $56 \text{ g mol}^{-1}$ ) (b) %  $\text{Fe}_3\text{O}_4$  ( $232 \text{ g mol}^{-1}$ )

**Plan** (a)  $\text{Fe}^{2+}$  is oxidised to  $\text{Fe}^{3+}$  by  $\text{MnO}_4^-$  in acidic medium.



From the stoichiometric ratio, on comparison, moles of Fe hence, its amount (in gram) is calculated. Thus % of Fe is also determined.



Knowing number of moles of  $\text{Fe}_3\text{O}_4$  which is equivalent to 3 mol  $\text{MnO}_4^-$ , its % can be determined.

**Solution** Moles of  $\text{MnO}_4^- = \frac{\text{molarity} \times \text{volume (in mL)}}{1000}$



$$\therefore \frac{47.22 \times 0.02242}{1000} \text{ mol MnO}_4^-$$

$$= \frac{5 \times 47.22 \times 0.02242}{1000} \text{ mol Fe}^{2+}$$

$$= 0.00529 \text{ mol Fe}^{2+}$$

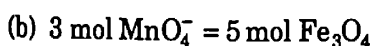
$$= 0.00529 \times 56$$

$$= 0.2964 \text{ g Fe}^{2+}$$

Thus, % of pure  $\text{Fe}(\text{Fe}^{2+})$  in 0.8040 g sample

$$= \frac{0.2964}{0.8040} \times 100$$

$$= 36.87\%$$



$$\therefore \frac{47.22 \times 0.02242}{1000} \text{ mol MnO}_4^-$$

$$= \frac{5}{3} \times \frac{47.22 \times 0.02242}{1000} \text{ mol}$$

$$= 0.001764 \text{ mol Fe}_3\text{O}_4$$

$$= 0.001764 \times 232 \text{ g Fe}_3\text{O}_4$$

$$= 0.4094 \text{ g}$$

$$\% \text{ as Fe}_3\text{O}_4 = \frac{0.4094}{0.8040} \times 100$$

$$= 50.91\%$$

**Problem 15.** 25 mL of a solution containing 6.1 g  $\text{L}^{-1}$  of an oxalate of formula  $\text{K}_x\text{H}_y(\text{C}_2\text{O}_4)_z \cdot n\text{H}_2\text{O}$  required 18 mL of 0.1 N NaOH and 24 mL of 0.1 N  $\text{KMnO}_4$  in two separate titrations. What is the compound?

**Plan**  $\text{K}_x\text{H}_y(\text{C}_2\text{O}_4)_z \cdot n\text{H}_2\text{O}$  has  $y$  ionisable  $\text{H}^+$  ions determined by NaOH and  $z$  oxidisable  $\text{C}_2\text{O}_4^{2-}$  ions determined by  $\text{MnO}_4^-$ ,  $\text{K}^+$  and  $\text{H}^+$  both are monovalent cations and  $\text{C}_2\text{O}_4^{2-}$  is divalent anion hence,  $x + y = 2z$

Thus, from three linear equations, value of  $x$ ,  $y$  and  $z$  can be determined. Value of  $n$  is determined when molecular weight of the compound is also known.

**Solution** Concentration = 6.1 g/L

$\text{K}^+$  and  $\text{H}^+$  are cations and oxalate  $\text{C}_2\text{O}_4^{2-}$  is an anion

$$\text{hence,} \quad x + y = 2z \quad \dots(i)$$

(a) NaOH will neutralize  $\text{H}^+$  part

25 mL of  $N_1$  (acid oxalate) = 18 mL of 0.1 N NaOH

$$\therefore N_1 \text{ (acid oxalate)} = \frac{18 \times 0.1}{25} = 0.072 \text{ N}$$

$$\text{Eq. wt. of an acid salt} = \frac{6.1}{0.072} = 84.72 \text{ g equiv}^{-1}$$

(b)  $\text{KMnO}_4$  will oxidise  $\text{C}_2\text{O}_4^{2-}$

$\therefore 25 \text{ mL } N_1' (\text{C}_2\text{O}_4^{2-}) \equiv 24 \text{ mL of } 0.01 \text{ N } \text{KMnO}_4$

$$N_1' (\text{C}_2\text{O}_4^{2-}) = 0.096 \text{ N}$$

$$\text{Eq. wt. of oxalate (reducing agent)} = \frac{6.1}{0.096} = 63.54$$

$$\text{Thus, } \frac{\text{mol. wt.}}{y} = \text{eq. wt. (84.72) when it is an acid salt}$$

$$\frac{\text{mol. wt.}}{2z} = \text{eq. wt. (63.54)}$$

when it is a reducing agent

$$\therefore \frac{2z}{y} = \frac{84.72}{63.54}$$

$$\therefore y = 1.5z \quad \dots(ii)$$

Using Eqs. (i) and (ii),  $x + 1.5z = 2z$

$$x = 0.5z$$

$\therefore x, y$  and  $z$  are in the ratio of 1 : 3 : 2 (to balance charge)

$$\text{or} \quad x = 1, \quad y = 3, \quad z = 2$$

$$\therefore \text{Mol. wt.} = 84.72 \times 3 = 254.16$$

$$39x + y + 88z + 18n = 254.16$$

$$\therefore n = 2$$

hence, salt is  $\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ .

**Problem 16.** 30 mL of an acidified solution of 1.5 N  $\text{MnO}_4^-$  ions, 15 mL of 0.5 N oxalic acid and 15 mL of 0.4 N ferrous salt solution are added together. Find the molarities of  $\text{MnO}_4^-$  and  $\text{Fe}^{3+}$  ions in the final solution.

**Plan**  $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  is oxidised to  $\text{Fe}^{3+}$  and  $\text{C}_2\text{O}_4^{2-}$  is oxidised to  $\text{CO}_2$

$$\text{molarity} = \frac{\text{normality}}{\text{change in oxidation number}}$$

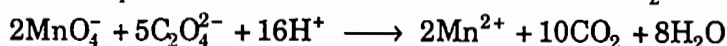
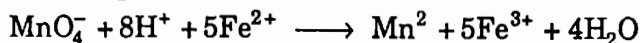
$$\therefore M(\text{MnO}_4^-) = \frac{N}{5} (\text{MnO}_4^-)$$

$$M(\text{Fe}^{2+}) = N(\text{Fe}^{2+})$$

$$M(\text{C}_2\text{O}_4^{2-}) = \frac{N}{2} (\text{C}_2\text{O}_4^{2-})$$

On comparison of milliequivalents of each reactant, final concentration of  $\text{Fe}^{3+}$  and  $\text{MnO}_4^-$  can be calculated.

**Solution** Acidified  $\text{MnO}_4^-$  oxidises  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$  and  $\text{C}_2\text{O}_4^{2-}$  into  $\text{CO}_2$ .



$$\text{Milliequivalents of } \text{MnO}_4^- = 30 \times 1.5 = 45$$

$$\text{Milliequivalents of } \text{Fe}^{2+} = 15 \times 0.4 = 6.0$$

$$\text{Milliequivalents of oxalic acid} = 15 \times 0.5 = 7.5$$

Milliequivalents of  $\text{MnO}_4^-$  used by 6.0 milliequivalents of

$$\text{Fe}^{2+} = 6.0$$

milliequivalents of  $\text{MnO}_4^-$  used by 6.5 milliequivalents of oxalic acid = 7.5

thus, total milliequivalents of  $\text{MnO}_4^-$  used = 13.5

$$\text{milliequivalents of } \text{MnO}_4^- \text{ left} = 45 - 13.5$$

$$= 31.5 \text{ in } 60 \text{ mL}$$

$$\text{thus, } [\text{MnO}_4^-] = \frac{31.5 \times 10^{-3} \times 1000 \text{ N}}{60} = \frac{31.5}{60} \text{ N}$$

$$= \frac{31.5}{60} \times \frac{1}{5} \text{ M} = 0.105 \text{ M}$$

Milliequivalents of  $\text{Fe}^{2+}$  consumed

$$= \text{milliequivalents of } \text{Fe}^{3+} \text{ formed}$$

$$= 6.0 \text{ in } 60 \text{ mL solution}$$

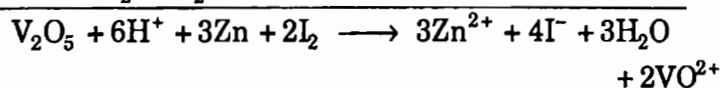
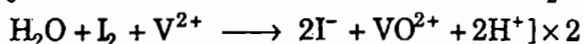
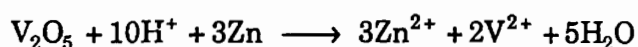
$$\text{thus, } [\text{Fe}^{3+}] = \frac{6.0}{60} \times 10^{-3} \times 1000 \text{ N} = 0.1 \text{ N}$$

$$= 0.1 \text{ M}$$

**Problem 17.** If 10 g of  $\text{V}_2\text{O}_5$  is dissolved in acid and is reduced to  $\text{V}^{2+}$  by zinc metal, how many moles of  $\text{I}_2$  could be reduced by the resulting solution if it is further oxidised to  $\text{VO}^{2+}$  ions? ( $V = 51, O = 16, I = 127$ )

**Plan** From the stoichiometric coefficients, number of moles of  $\text{I}_2$  reduced by given amount of  $\text{V}_2\text{O}_5$  can be determined.

**Solution**



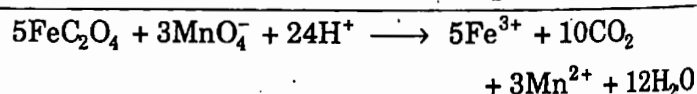
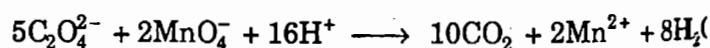
Thus, 1 mol of  $\text{V}_2\text{O}_5$  reduces = 2 mol of  $\text{I}_2$

$$\begin{aligned} \text{hence, } 10 \text{ g} &= \frac{10}{182} \text{ mol of } \text{V}_2\text{O}_5 \text{ reduces} \\ &= 2 \times \frac{10}{182} \text{ mol of } \text{I}_2 \\ &= 0.11 \text{ mol of } \text{I}_2 \end{aligned}$$

**Problem 18.** 1.44 g pure  $\text{FeC}_2\text{O}_4$  was dissolved in dil. HCl and solution diluted to 100 mL. Calculate volume of 0.01 M  $\text{KMnO}_4$  required to oxidise  $\text{FeC}_2\text{O}_4$  solution completely.

**Plan**  $\text{MnO}_4^-$  oxidises  $\text{Fe}^{2+}$  as well as  $\text{C}_2\text{O}_4^{2-}$ . Thus, from the number of moles of  $\text{Fe}^{2+}$  and  $\text{C}_2\text{O}_4^{2-}$  number of moles hence volume of  $\text{MnO}_4^-$  can be determined.

**Solution**  $\text{Fe}^{2+}$  is oxidised to  $\text{Fe}^{3+}$  and  $\text{C}_2\text{O}_4^{2-}$  is oxidised to  $\text{CO}_2$  by  $\text{MnO}_4^-$  in acidic medium.



Thus, 5 mol of  $\text{FeC}_2\text{O}_4$  are oxidised by = 3 mol of  $\text{MnO}_4^-$

1.44 g (= 0.01 mol)  $\text{FeC}_2\text{O}_4$  is oxidised by

$$= \frac{3}{5} \times 0.01 = 0.006 \text{ mol } \text{MnO}_4^-$$

If V mL of 0.01 M  $\text{KMnO}_4$  are required then

$$\frac{0.01 \times V}{1000} = 0.006$$

$\therefore$

$$V = 600 \text{ mL}$$

$$(\text{moles} = \frac{mV}{1000} = \frac{0.01 \times V}{1000} = 0.006)$$

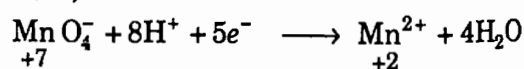
**Problem 19.** For titrating a certain volume of reducing substance by 1 M  $\text{KMnO}_4$ , it is found that 20 mL was used in acidic medium, 33.4 mL was used in alkaline medium and 100 mL was used in neutral medium.  $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$  in acidic medium, to what state is  $\text{MnO}_4^-$  reduced to in alkaline and neutral medium?

**Plan** From the volume of  $\text{MnO}_4^-$  used in acidic medium normality of  $\text{MnO}_4^-$  in basic medium as well as in neutral medium can be determined. Since

$$\text{normality} = \text{molarity} \times \text{change in O.N.}$$

hence, O.N. of Mn in final state is known.

**Solution** In acidic medium  $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$  (by gain of  $5e^-$ )



thus,

$$1 \text{ M } \text{MnO}_4^- = 5 \text{ N } \text{MnO}_4^-$$

(normality = molarity  $\times$  change in oxidation number)

Let normality in alkaline medium be  $N'$  and in neutral medium  $N''$

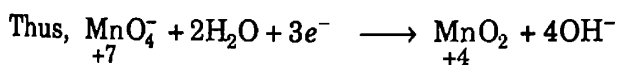
$$20 \text{ mL of } 5 \text{ N MnO}_4^- \equiv 33.4 \text{ mL } N' \text{ MnO}_4^- \\ \equiv 100 \text{ mL of } N'' \text{ MnO}_4^-$$

$$\therefore N' (\text{alkaline}) = 3 \text{ N}$$

$$N'' (\text{neutral}) = 1 \text{ N}$$

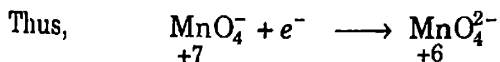
Thus, change in oxidation number in alkaline medium = 3

Hence,  $\text{MnO}_4^-$  is reduced to  $\text{MnO}_2$  (+4)



$\text{MnO}_4^-$  is reduced to  $\text{MnO}_4^{2-}$  (+6) in neutral medium

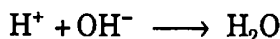
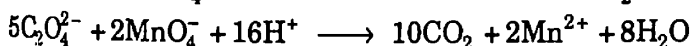
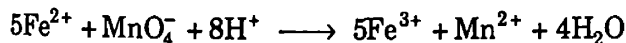
when change in oxidation number is one unit :



**Problem 20.** If 1.00 mL  $\text{KMnO}_4$  solution will react with 0.125 g  $\text{Fe}^{2+}$  and if 1.00 mL of  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$  solution will react with 0.175 mL of  $\text{KMnO}_4$  solution, how many millilitres of 0.20 M  $\text{NaOH}$  will react with 1.00 mL of  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$  solution in which all the protons ( $\text{H}^+$ ) are ionisable? ( $\text{Fe} = 56 \text{ g mol}^{-1}$ )

*Plan* We are to relate oxidisable  $\text{C}_2\text{O}_4^{2-}$  ions with ionisable  $\text{H}^+$  ions in  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ . Molar concentration of  $\text{MnO}_4^-$  is determined by  $\text{Fe}^{2+}$ . In turn  $\text{C}_2\text{O}_4^{2-}$  is determined by  $\text{MnO}_4^-$ . Thus, number of ionisable  $\text{H}^+$  hence, volume of  $\text{NaOH}$  can be determined.

**Solution**



$$\text{Let molarity of } \text{MnO}_4^- \text{ solution} = M_1$$

$$\text{and molarity of } \text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \text{ solution} = M_2$$

$$\text{Number of moles of } \text{Fe}^{2+} = \frac{0.125}{56} \text{ mol}$$

$$\text{Number of moles of } \text{MnO}_4^- = \frac{1 \times M_1}{1000} = 0.001 M_1$$

$$\text{Also, } 5 \text{ mol of } \text{Fe}^{2+} = 1 \text{ mol } \text{MnO}_4^-$$

$$\therefore \frac{0.125}{56} \text{ mol of } \text{Fe}^{2+} = \frac{1}{5} \times \frac{0.125}{56} \text{ mol } \text{MnO}_4^-$$

$$\frac{0.125}{5 \times 56} = 0.001 M_1$$

$$\therefore M_1 (\text{MnO}_4^-) = 0.446 \text{ M}$$

$$\text{Also, } 1.00 \text{ mL of } M_2 \text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$$

$$\equiv 0.175 \text{ mL of } 0.446 \text{ M } \text{MnO}_4^-$$

$$1 \times M_2 \text{ millimol } \text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$$

$$= 0.001 M_2 \text{ mole of } \text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$$

$$= 0.002 M_2 \text{C}_2\text{O}_4^{2-} \text{ ions}$$

(since,  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$  has two oxidisable  $\text{C}_2\text{O}_4^{2-}$  ions)

$$5 \text{ mol of } \text{C}_2\text{O}_4^{2-} = 2 \text{ mol of } \text{MnO}_4^-$$

$$\therefore 0.002 M_2 \text{C}_2\text{O}_4^{2-} = \frac{2}{5} \times 0.002 M_2 \text{ MnO}_4^-$$

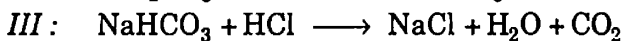
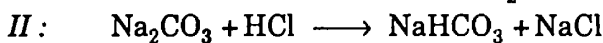
$$\therefore \frac{0.004}{5} M_2 = \frac{0.175 \times 0.446}{1000} \text{ mol } \text{MnO}_4^-$$

$$\therefore M_2 = \frac{0.175 \times 0.446 \times 5}{1000 \times 0.004}$$

$$M_2 (\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4) = 0.0976 \text{ M}$$

**Problem 21.** A mixture containing  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$  and inert matter weighs 0.7500 g. When the aqueous solution is titrated with 0.5000 N  $\text{HCl}$ , the colour of the phenolphthalein disappears when 21.00 mL of the acid has been added. Methyl orange is then added and 7.00 mL more of the acid is required to give a red colour to the solution. Find the percentage composition of the sample.

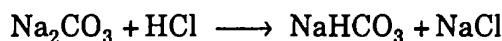
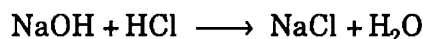
*Plan* Phenolphthalein indicates complete reaction of  $\text{NaOH}$  and 50% reaction of  $\text{Na}_2\text{CO}_3$ . Remaining 50% reaction of  $\text{Na}_2\text{CO}_3$  is indicated when methyl orange is added at this stage. Thus, from the volume of  $\text{HCl}$ , % of each is determined.



**Solution** Let volume of 0.5000 N  $\text{HCl}$  for complete neutralisation of  $\text{NaOH} = x \text{ mL}$

$$\text{and for that of } \text{Na}_2\text{CO}_3 = y \text{ mL}$$

Phenolphthalein indicates 100% reaction of  $\text{NaOH}$  but 50% reaction of  $\text{Na}_2\text{CO}_3$  upto  $\text{NaHCO}_3$  stage.



On the other hand, methyl orange indicates 100% reaction each of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$  both.

Thus, first end-point appears when complete  $\text{NaOH}$  and 50%  $\text{Na}_2\text{CO}_3$  have reacted (stage I and II)

$$\text{thus, } x + \frac{y}{2} = 21.00 \text{ mL}$$

Second end-point appears when remaining  $\text{Na}_2\text{CO}_3$  reacts.

$$\text{thus, } \frac{y}{2} = 7 \text{ mL, } y = 14 \text{ mL}$$

$$\text{hence, } x = 14 \text{ mL}$$

$$\text{thus, } 14 \text{ mL of } 0.5000 \text{ N HCl} \equiv \text{NaOH}$$

$$\text{thus, NaOH in mixture} = \frac{14 \times 0.5}{1000} = 7 \times 10^{-3} \text{ equivalent} \\ = 7 \times 10^{-3} \times 40 = 0.28 \text{ g NaOH}$$

Similarly, 14 mL of 0.5000 N  $\text{HCl}$

$$\equiv \text{Na}_2\text{CO}_3 = 7 \times 10^{-3} \text{ equivalent}$$

$$= 7 \times 10^{-3} \times 53 \text{ g} = 0.371 \text{ g Na}_2\text{CO}_3$$

$$\% \text{ of NaOH in mixture} = \frac{0.28}{0.75} \times 100 = 37.33\%$$

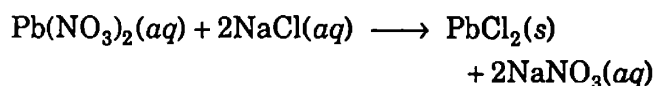
$$\% \text{ of Na}_2\text{CO}_3 \text{ in mixture} = \frac{0.371}{0.750} \times 100 = 49.47\%$$

# Master Exercises

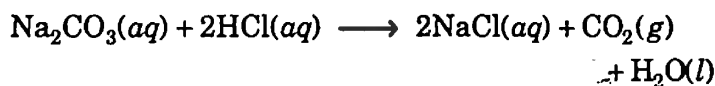
## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

1. What volume of 0.125 M NaOH, in mL contains 4.0 g of NaOH?
2. If 1.06 g of  $\text{Na}_2\text{CO}_3$  is dissolved in enough water to make 250 mL of solution, what is molar concentration of  $\text{Na}_2\text{CO}_3$ ? What are molar concentrations of  $\text{Na}^+$  and  $\text{CO}_3^{2-}$  ions?
3. For each solution, identify the ions that exist in aqueous solution, and specify the concentration of each ion  
(a) 0.25 M  $(\text{NH}_4)_2\text{SO}_4$       (b) 0.123 M  $\text{Na}_2\text{CO}_3$   
(c) 0.056 M  $\text{HNO}_3$
4. If you dilute 25.0 mL of 1.50 M HCl to 500 mL, what is molar concentration of the dilute acid?
5. Which of the following methods would you use to prepare 1.00 L of 0.125 M  $\text{H}_2\text{SO}_4$ ?  
(a) Dilute 20.8 mL of 6.00 M  $\text{H}_2\text{SO}_4$  to a volume of 1.00 L.  
(b) Add 950 mL of water to 50.0 mL of 3.00 M  $\text{H}_2\text{SO}_4$ .
6. What volume of 0.750 M  $\text{Pb}(\text{NO}_3)_2$  is mL, is required to react completely with 1.00 L of 0.225 M NaCl solution?



7. If 38.55 mL of HCl is required to titrate 2.150 g of  $\text{Na}_2\text{CO}_3$  as given, what is the concentration ( $\text{mol L}^{-1}$ ) of the HCl solution?

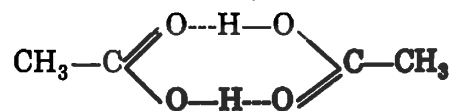


8. You have 0.490 g of unknown acid,  $\text{H}_2\text{A}$ , which reacts with KOH, according to



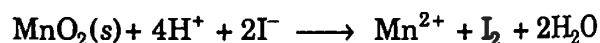
If 100 mL of 0.1 M KOH is required to titrate the acid to the second equivalence point, what is the molar mass of acid?

9. In which of the following cases, equilibrium molarity and analytical molarity are identical?  
(a) 1 M glucose solution  
(b) 1 M  $\text{H}_3\text{PO}_4$  solution  
(c) saturated AgI solution  
(d) solution of LiCl in ether.
10. Acetic acid forms 100% dimer in benzene by hydrogen bonding as shown below by --- lines.



If analytical molarity is 1 M, what is its equilibrium molarity?

11. Calculate the percentage of  $\text{MnO}_2$  in a mineral specimen if the iodine liberated by a 0.1344 g sample in the net reaction



required 32.30 mL of 0.07220 M  $\text{Na}_2\text{S}_2\text{O}_3$ . ( $\text{MnO}_2 = 87 \text{ g mol}^{-1}$ )

### Analytical Questions

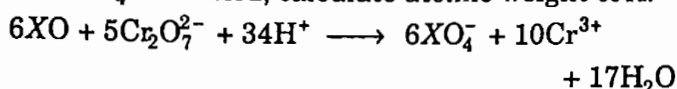
1. A  $5.00 \times 10^2$  mL sample of 2.00 M HCl is treated with 4.47 g of magnesium. Calculate the concentration of the acid solution after all the metal has reacted. Assume that the volume remains unchanged.
2. A useful application of oxalic acid is the removal of rust ( $\text{Fe}_2\text{O}_3$ ) from a cloth:  
$$\text{Fe}_2\text{O}_3(s) + 6\text{H}_2\text{C}_2\text{O}_4 \longrightarrow 2\text{Fe}(\text{C}_2\text{O}_4)_3^{3-} + 3\text{H}_2\text{O} + 6\text{H}^+$$
  
Calculate the number of grams of rust that can be removed by  $5.00 \times 10^2$  mL of 1 M oxalic acid.
3. 30 mL of  $x$  M HCl neutralise completely 10 mL of 0.2 M  $\text{NaHCO}_3$  and further 5 mL of 0.2 M  $\text{Na}_2\text{CO}_3$  to phenolphthalein end-point. What is value of  $x$ ?

4. 300 mL of  $\text{H}_2\text{SO}_4$  solution of a certain molarity was mixed with 200 mL of a  $\text{Ba}(\text{OH})_2$  solution of same molarity. The pH of the mixture solution is 1. Calculate normality of  $\text{H}_2\text{SO}_4$  and  $\text{Ba}(\text{OH})_2$ .
5. What volume of 6M NaOH would be required to react with the  $\text{SO}_2$  produced from  $10^3$  kg of coal containing 0.05% by mass of  $\text{FeS}_2$  (iron pyrites).
 
$$2\text{FeS}_2 + 5.5 \text{O}_2 \longrightarrow \text{Fe}_2\text{O}_3 + 4\text{SO}_2$$

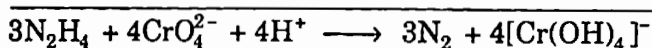
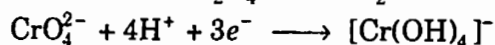
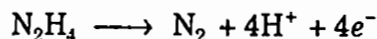
$$\text{SO}_2 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$$
6. 25 mL solution containing a mixture of  $\text{Na}_2\text{CO}_3$  and NaOH required 19.5 mL of 0.995 N HCl for the phenolphthalein end-point and in a separate titration 25 mL of the same mixture required 25.9 mL of same HCl for methyl orange end-point. Calculate concentration of each base in mixture.
7. A drop (0.05 mL) of 12.0 M HCl is spread over a sheet of thin aluminium foil. Assuming that all the acid dissolves through the foil, what will be the area, in  $\text{cm}^2$ , of the hole produced? (density of Al =  $2.70 \text{ g cm}^{-3}$ ; thickness of the foil = 0.10 mm)
8. Titration of a 0.7439 g sample of impure  $\text{Na}_2\text{B}_4\text{O}_7$  (borax) required 31.64 mL of 0.108 M HCl for reaction. Express the result of this analysis in terms of per cent (B = 11)
  - (a)  $\text{Na}_2\text{B}_4\text{O}_7$
  - (b)  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
  - (c)  $\text{B}_2\text{O}_3$
  - (d) B
$$\text{B}_4\text{O}_7^{2-} + 2\text{H}_3\text{O}^+ + 3\text{H}_2\text{O} \longrightarrow 4\text{H}_3\text{BO}_3$$
9. Average human blood serum contains 18 mg of  $\text{K}^+$  and 365 mg of  $\text{Cl}^-$  per 100 mL. Calculate
  - (a) the molar concentration for each of these species; use  $1.00 \text{ g mL}^{-1}$ , for the density of the serum
  - (b)  $p_{\text{K}^+}$  and  $p_{\text{Cl}^-}$  for human serum.
10. A mixture of HCl and  $\text{H}_3\text{PO}_4$  is titrated with 0.1 M NaOH. The first end-point (methyl red) occurs at 35.00 mL and the second end-point (bromothymol blue) occurs at a total of 50.00 mL (15.00 mL after the first end-point). Calculate the millimoles of HCl and  $\text{H}_3\text{PO}_4$  present in the solution.
11. A sample of  $\text{P}_2\text{O}_5$  contains some  $\text{H}_3\text{PO}_4$  impurity. A 0.405 g sample is reacted with water ( $\text{P}_2\text{O}_5 + 3\text{H}_2\text{O} \longrightarrow 2\text{H}_3\text{PO}_4$ ), and the resulting solution is titrated with 0.25 M NaOH requiring 42.5 mL (upto  $\text{Na}_2\text{HPO}_4$ ). What is the per cent  $\text{H}_3\text{PO}_4$  impurity?
12. 1.2 g sample of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  was dissolved in water to form 100 mL of solution. 20 mL of this solution required 40 mL of 0.1 N HCl for complete neutralisation. Calculate the weight of  $\text{Na}_2\text{CO}_3$  in mixture. If another 20 mL of this solution is treated with excess of  $\text{BaCl}_2$ , what will be the weight of the precipitate?
13. 2.4 g of a mixture of (KCl +  $\text{NH}_4\text{Cl}$ ) is heated till constant weight is obtained. The solid residue is dissolved in water and the solution is made up to 250 mL. 25 mL of this solution required 15 mL of 0.1 N  $\text{AgNO}_3$  for precipitation of chloride. Calculate percentage of chloride by weight in the mixture.
14. The concentration of  $\text{Cu}^{2+}$  ions in the water discharged from a certain industrial plant is determined by adding excess sodium sulphide solution to 0.80 L of water.
 
$$\text{S}^{2-} + \text{Cu}^{2+} \longrightarrow \text{CuS(s)}$$
 What is molar concentration of  $\text{Cu}^{2+}$  in water sample if 0.0177 g of solid CuS is formed?
15.  $\text{Mn}^{2+}(\text{aq})$  can be determined by titration with  $\text{MnO}_4^-(\text{aq})$ .
 
$$\text{Mn}^{2+} + \text{MnO}_4^- + \text{OH}^- \longrightarrow \text{MnO}_2 + \text{H}_2\text{O} \text{ (unbalanced)}$$
 A 25.00 mL sample of  $\text{Mn}^{2+}(\text{aq})$  requires 34.77 mL of 0.05876 M  $\text{KMnO}_4(\text{aq})$  for its titration. What is the molarity of the  $\text{Mn}^{2+}(\text{aq})$ ?
16. Oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) is present in many plants and vegetables. If 24.0 mL of 0.01 M  $\text{KMnO}_4$  solution is needed to titrate 1.00 g of  $\text{H}_2\text{C}_2\text{O}_4$  to the equivalence-point, what is the per cent by mass of  $\text{H}_2\text{C}_2\text{O}_4$  in the sample?
17. The calcium oxalate isolated from blood is dissolved in acid and titrated against a standardised  $\text{KMnO}_4$  solution. In one test, it is found that the calcium oxalate isolated from a 10.0 mL sample of blood requires 24.2 mL of  $9.56 \times 10^{-4}$  M  $\text{KMnO}_4$  for titration. Calculate the number of milligrams of calcium per mL of blood.
18. A solution contains 2.52 g of a reductant per litre. 25 mL of this solution of the reductant required 20 mL of 0.01 M  $\text{KMnO}_4$  in acidic medium for oxidation. Find the molecular weight of the reductant given that each of the two atoms which undergo oxidation per molecule of the reductant, suffers an increase in the oxidation state by one unit.
19. In an experiment 10 L of air (containing  $\text{O}_3$ ) at 1 atm and  $27^\circ\text{C}$  were passed through an alkaline KI solution. After neutralisation, free iodine required 1.5 mL of 0.01 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Calculate mol% of  $\text{O}_3$  in air.
20. A polyvalent metal weighing 0.1 g and having atomic weight 51 reacted with dil.  $\text{H}_2\text{SO}_4$  to give 43.9 mL of  $\text{H}_2$  at STP. This solution containing the metal in lower oxidation state is found to require 58.8 mL of 0.1 N  $\text{KMnO}_4$  for complete oxidation. What are the oxidation states of the metal in two reactions?



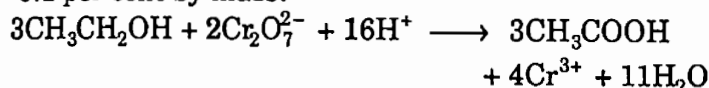
21. 0.015 mol of  $K_2Cr_2O_7$  oxidises 2.18 g of a mixture of  $XO$  and  $X_2O_3$  into  $XO_4^-$  in acidic medium. If 0.0187 mol of  $XO_4^-$  is formed, calculate atomic weight of  $X$ .



22. What mass of  $N_2H_4$  can be oxidised to  $N_2$  by 24.0 g of  $K_2CrO_4$  which is reduced to  $[Cr(OH)_4]^-$ ?

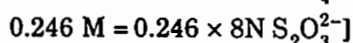
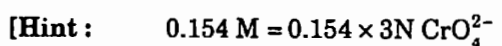


23. The alcohol content in a 10.0 g sample of blood from a driver required 4.23 mL of 0.07654 M  $K_2Cr_2O_7$  for titration. Should the police prosecute the individual for drunken-driving when the current legal limit is 0.1 per cent by mass?



24. A 1 g sample of  $H_2O_2$  solution containing  $x$  per cent  $H_2O_2$  by weight required  $x$  mL of  $KMnO_4$  solution for complete oxidation in acidic medium. Calculate normality of  $KMnO_4$  solution.

25. In basic solution  $CrO_4^{2-}$  oxidises  $S_2O_3^{2-}$  to form  $Cr(OH)_4^-$  and  $SO_4^{2-}$ . How many mL of 0.154 M  $CrO_4^{2-}$  are required to react with 40.0 mL of 0.246 M  $S_2O_3^{2-}$ ?



26. 25 mL of a solution containing ferrous sulphate and ferric sulphate acidified with  $H_2SO_4$  is reduced by metallic zinc. The solution required 34.25 mL of 0.1 N solution of  $K_2Cr_2O_7$  for oxidation. However, before reduction with zinc, 25 mL of same solution required 22.45 mL of same  $K_2Cr_2O_7$ . Calculate the weight of  $FeSO_4$  and  $Fe_2(SO_4)_3$  per litre of the solution.

27. (a) The ion  $A^{n+}$  is oxidised to  $AO_3^-$  by  $MnO_4^-$  changing to  $Mn^{2+}$  in acid solution. Given that  $2.68 \times 10^{-3}$  mol of  $A^{n+}$  requires  $1.61 \times 10^{-3}$  mol of  $MnO_4^-$ , what is the value of  $n$ ?

- (b) What is the weight of one-gram equivalent  $ACl_n$  for the above reaction if the atomic mass of  $A$  is 97.0?

28. 0.518 g sample of limestone is dissolved and calcium is precipitated as calcium oxalate  $CaC_2O_4$ . After filtration and washing the precipitate, it requires 40 mL of 0.05 M  $KMnO_4$  solution acidified with sulphuric acid to titrate it. What is the percentage of  $CaO$  in the limestone?

29. 20 mL of a solution containing 0.2 g of impure sample of  $H_2O_2$  reacts with 0.316 g of  $KMnO_4$  in presence of  $H_2SO_4$ .

- (a) What is % purity of  $H_2O_2$ ?

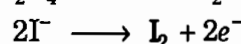
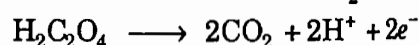
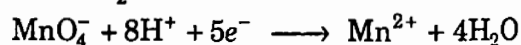
- (b) Calculate the volume of dry  $O_2$  formed at  $27^\circ C$  and 750 mmHg pressure.

30.  $Na_2C_2O_4$  and  $KHC_2O_4 \cdot H_2C_2O_4$  are mixed in such proportion by weight that the normality of the resulting solution as a reducing agent is 3.62 times the normality as an acid. What is the proportion?

31. A standard solution of potassium dichromate contains  $5.442 \text{ g L}^{-1}$ . What is the amount in terms of  $Fe_3O_4$  per mL  $K_2Cr_2O_7$ ?

32. A 0.5 g sample containing  $MnO_2$  is treated with  $HCl$  liberating  $Cl_2$ . The  $Cl_2$  is passed into a solution of  $I^-$  and 30.0 mL of 0.1 M  $Na_2S_2O_3$  are required to titrate the liberated iodine. Calculate the percentage of  $MnO_2$  in the sample. ( $Mn = 55$ )

33. Calculate the mass of oxalic acid,  $H_2C_2O_4$ , which can be oxidised to  $CO_2$  by 100 mL of an  $MnO_4^-$  solution of 10 mL of which is capable of oxidising 50.0 mL of 1.00 N  $I^-$  to  $I_2$



34. 5.0 g of bleaching powder was suspended in water and the volume made up to half a litre. 20 mL of this suspension when acidified with acetic acid and treated with excess of potassium iodide solution liberated iodine which required 20 mL of a decinormal hypo solution for titration. Calculate the percentage of available chlorine in bleaching powder.

## Exercise 2

### (Stage 2 : High Skill Problem Solving)

#### Only One Option Correct

1. To prepare a solution that is 0.50 M  $KCl$  starting with 100 mL of 0.40 M  $KCl$
- (a) add 0.75 g  $KCl$  (b) add 20 mL of water  
(c) add 0.10 mol  $KCl$  (d) evaporate 10 mL water

2. 10.78 g of  $H_3PO_4$  in 550 mL solution is 0.40 N. This acid
- (a) has been neutralised to  $HPO_4^{2-}$   
(b) has been neutralised to  $PO_4^{3-}$   
(c) has been reduced to  $H_2PO_2^-$   
(d) has been neutralised to  $H_2PO_4^-$

3. How many equivalents are there per mol of  $\text{H}_2\text{S}$  in its oxidation to  $\text{SO}_2$ ?  
 (a) 2 (b) 4  
 (c) 6 (d) 8
4. In hot alkaline solution,  $\text{Br}_2$  disproportionates to  $\text{Br}^-$  and  $\text{BrO}_3^-$   

$$3\text{Br}_2 + 6\text{OH}^- \longrightarrow 5\text{Br}^- + \text{BrO}_3^- + 3\text{H}_2\text{O}$$
 hence, equivalent weight of  $\text{Br}_2$  is (molecular weight =  $M$ )  
 (a)  $\frac{M}{6}$  (b)  $\frac{M}{5}$   
 (c)  $\frac{3M}{5}$  (d)  $\frac{5M}{3}$
- [Hint : Each half-reaction, oxidation and reduction should involve equal number of electrons, balance it.  $3\text{Br}_2 \equiv 5e^-$ ]
5.  $M$  (molarity) and  $M'$  (molality) are related to each other by equation:  
 ( $m$  = molecular weight of solute,  $d$  = density g/mL)  
 (a)  $M \left( \frac{m}{1000} + \frac{1}{M'} \right) = d$  (b)  $M' = \left( \frac{1000 M}{1000 d - Mm} \right)$   
 (c) Both (a) and (b) (d) None of these
6. Maximum number of moles of  $\text{PbSO}_4$  that can be precipitated by mixing 20.00 mL of 0.1 M  $\text{Pb}(\text{NO}_3)_2$  and 30.00 mL of 0.1 M  $\text{Na}_2\text{SO}_4$  will be  
 (a) 0.002 (b) 0.003  
 (c) 0.005 (d) 0.001
7.  $[\text{Na}^+]$  in a solution prepared by mixing 30.00 mL of 0.12 M  $\text{NaCl}$  with 70 mL of 0.15 M  $\text{Na}_2\text{SO}_4$  is  
 (a) 0.135 M (b) 0.141 M  
 (c) 0.210 M (d) 0.246 M
8. When 80 mL of 0.20 M  $\text{HCl}$  is mixed with 120 mL of 0.15 M  $\text{KOH}$ , the resultant solution is the same as a solution of  
 (a) 0.16 M  $\text{KCl}$  and 0.02 M  $\text{HCl}$   
 (b) 0.08 M  $\text{KCl}$   
 (c) 0.08 M  $\text{KCl}$  and 0.01 M  $\text{KOH}$   
 (d) 0.08 M  $\text{KCl}$  and 0.01 M  $\text{HCl}$
9. Equal volumes of 0.200 M  $\text{HCl}$  and 0.400 M  $\text{KOH}$  are mixed. The concentration of the principal ions in the resulting solution are :  
 (a)  $[\text{K}^+] = 0.400 \text{ M}$ ,  $[\text{Cl}^-] = 0.200 \text{ M}$ ,  $[\text{H}^+] = 0.200 \text{ M}$   
 (b)  $[\text{K}^+] = 0.200 \text{ M}$ ,  $[\text{Cl}^-] = 0.200 \text{ M}$ ,  $[\text{OH}^-] = 0.100 \text{ M}$   
 (c)  $[\text{K}^+] = 0.200 \text{ M}$ ,  $[\text{Cl}^-] = 0.100 \text{ M}$ ,  $[\text{OH}^-] = 0.100 \text{ M}$   
 (d)  $[\text{K}^+] = 0.200 \text{ M}$ ,  $[\text{Cl}^-] = 0.100 \text{ M}$ ,  $[\text{OH}^-] = 0.200 \text{ M}$
10. Mass of  $\text{KHC}_2\text{O}_4$  (potassium acid oxalate) required to reduce 100 mL of 0.02 M  $\text{KMnO}_4$  in acidic medium (to  $\text{Mn}^{2+}$ ) is  $x$  g, and to neutralise 100 mL of 0.05 M  $\text{Ca}(\text{OH})_2$  is  $y$  g then,  
 (a)  $x = y$  (b)  $2x = y$   
 (c)  $x = 2y$  (d) None of these
11.  $2\text{H}_2\text{O}_2(l) \longrightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$   
 100 mL of  $X$  molar  $\text{H}_2\text{O}_2$  gives 3 L of  $\text{O}_2$  gas under the condition when 1 mol occupies 24 L, value of  $X$  is  
 (a) 2.5 (b) 1.0  
 (c) 0.5 (d) 0.25
12. If equal volumes of 1 M  $\text{KMnO}_4$  and 1 M  $\text{K}_2\text{Cr}_2\text{O}_7$  solutions are allowed to oxidise  $\text{Fe}(\text{II})$  to  $\text{Fe}(\text{III})$ , then  $\text{Fe}(\text{II})$  oxidised will be  
 (a) more by  $\text{KMnO}_4$  (b) more by  $\text{K}_2\text{Cr}_2\text{O}_7$   
 (c) equal in both cases (d) data is incomplete
13. 100 mL of 1 M  $\text{KMnO}_4$  oxidised 100 mL of  $\text{H}_2\text{O}_2$  in acidic medium (when  $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$ ); volume of same  $\text{KMnO}_4$  required to oxidise 100 mL of  $\text{H}_2\text{O}_2$  in basic medium (when  $\text{MnO}_4^-$  is reduced to  $\text{MnO}_2$ ) will be  
 (a)  $\frac{100}{3}$  mL (b)  $\frac{500}{3}$  mL  
 (c)  $\frac{300}{5}$  mL (d) 100 mL
14. 10 mL of  $\text{H}_2\text{O}_2$  solution (volume strength =  $x$ ) required 10 mL of  $\frac{N}{0.56} \text{MnO}_4^-$  solution in acidic medium. Hence,  $x$  is  
 (a) 0.56 (b) 5.6  
 (c) 0.1 (d) 10.0
15. Aqueous solution of chloride of an element  $A$  containing  $1 \times 10^{-3}$  mol after complete hydrolysis required 30 mL of 0.1 M  $\text{AgNO}_3$  solution to form  $\text{AgCl}$ . Element  $A$  is  
 (a) Al (b) P  
 (c) Si (d) S
16. Molality of 18 M  $\text{H}_2\text{SO}_4$  ( $d = 1.8 \text{ g mL}^{-1}$ ) is  
 (a) 36 mol  $\text{kg}^{-1}$  (b) 200 mol  $\text{kg}^{-1}$   
 (c) 500 mol  $\text{kg}^{-1}$  (d) 18 mol  $\text{kg}^{-1}$
17. 10 L of hard water required 0.56 g of lime ( $\text{CaO}$ ) for removing hardness. Hence, temporary hardness in ppm of  $\text{CaCO}_3$  (parts per million i.e.  $10^6$ ) is  
 (a) 100 (b) 200  
 (c) 10 (d) 20
18. 1 g equivalent of a substance is the weight of that amount of a substance which is equivalent to  
 (a) 0.25 mol of  $\text{O}_2$  (b) 0.50 mol of  $\text{O}_2$   
 (c) 1 mol of  $\text{O}_2$  (d) 8 mol of  $\text{O}_2$
19. In an experiment, 50 mL of 0.1 M solution of a metallic salt reacted exactly with 25 mL of 0.1 M solution of sodium sulphite. In the reaction  $\text{SO}_3^{2-}$  is oxidised to  $\text{SO}_4^{2-}$ . If the original oxidation number of the metal in the salt was 3, what would be the new oxidation number of the metal?  
 (a) 0 (b) 1  
 (c) 2 (d) 4

20. 20 mL of  $x$  M HCl neutralises completely 10 mL of 0.1 M  $\text{NaHCO}_3$  and a further 5 mL of 0.2 M  $\text{Na}_2\text{CO}_3$  solution to methyl orange end-point. The value of  $x$  is  
 (a) 0.167 M (b) 0.133 M  
 (c) 0.150 M (d) 0.200 M
21. The molality of a  $\text{H}_2\text{SO}_4$  solution is 9. The weight of the solute in 1 kg  $\text{H}_2\text{SO}_4$  solution is  
 (a) 900.0 g (b) 468.65 g  
 (c) 882.0 g (d) 9.0 g
22. The density of 1 M solution of NaCl is 1.0585 g/mL. The molality of the solution is  
 (a) 1.0585 (b) 1.00  
 (c) 0.10 (d) 0.0585
23. Which is not true about  $\text{H}_3\text{PO}_2$ ?  
 (a) It is tribasic acid  
 (b) One mol is neutralised by 0.5 mol  $\text{Ca}(\text{OH})_2$   
 (c)  $\text{NaH}_2\text{PO}_2$  is normal salt  
 (d) It disproportionates to  $\text{H}_3\text{PO}_3$  and  $\text{PH}_3$  on heating
24.  $\text{RH}_2$  (ion exchange resin) can replace  $\text{Ca}^{2+}$  in hard water  

$$\text{RH}_2 + \text{Ca}^{2+} \longrightarrow \text{RCa} + 2\text{H}^+$$
 1 L of hard water after passing through  $\text{RH}_2$  has pH 2. Hence, hardness in ppm of  $\text{Ca}^{2+}$  is  
 (a) 200 (b) 100  
 (c) 50 (d) 125
25. 1 mol  $\text{BaF}_2 + 2$  mol  $\text{H}_2\text{SO}_4 \longrightarrow$  resulting mixture will be neutralised by  
 (a) 1 mol KOH  
 (b) 2 mol  $\text{Ca}(\text{OH})_2$   
 (c) 3 mol NaOH  
 (d) 2 mol KOH
26. 100 mL of a mixture of NaOH and  $\text{Na}_2\text{SO}_4$  is neutralised by 10 mL of 0.5 M  $\text{H}_2\text{SO}_4$ . Hence, amount of NaOH in 100 mL mixture is  
 (a) 0.2 g (b) 0.4 g  
 (c) 0.6 g (d) 1.0 g
27. 10 mL of  $\text{NaHC}_2\text{O}_4$  solution is neutralised by 10 mL of 0.1 M NaOH solution. 10 mL of same  $\text{NaHC}_2\text{O}_4$  solution is oxidised by 10 mL of  $\text{KMnO}_4$  solution in acidic medium. Hence, molarity of  $\text{KMnO}_4$  is  
 (a) 0.1 M (b) 0.2 M  
 (c) 0.04 M (d) 0.02 M
28. For a given mixture of  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$ , volume of a given HCl required is  $x$  mL with phenolphthalein indicator and further  $y$  mL required with methyl orange indicator. Hence, volume of HCl for complete reaction of  $\text{NaHCO}_3$  is  
 (a)  $2x$  (b)  $\frac{x}{2}$   
 (c)  $y$  (d)  $(y - x)$
29. 1 mol of ferric oxalate is oxidised by  $x$  mol of  $\text{MnO}_4^-$  and also 1 mol of ferrous oxalate is oxidised by  $y$  mol  $\text{MnO}_4^-$  in acidic medium. The ratio  $\frac{x}{y}$  is  
 (a) 2 : 1 (b) 1 : 2  
 (c) 3 : 1 (d) 1 : 3
30. 40 mL of 0.05 M solution of sesquicarbonate ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ) is titrated against 0.05 M HCl.  $x$  mL of HCl is used when phenolphthalein is the indicator and  $y$  mL of HCl is used when methyl orange is the indicator in two separate titrations, hence  $(y - x)$  is  
 (a) 80 mL (b) 30 mL  
 (c) 120 mL (d) None of these
31. 3 moles of a mixture of  $\text{FeSO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$  require 100 mL of 2 M  $\text{KMnO}_4$  solution in acidic medium. Hence, mole fraction of  $\text{FeSO}_4$  in the mixture is  
 (a)  $\frac{1}{3}$  (b)  $\frac{2}{3}$   
 (c)  $\frac{2}{5}$  (d)  $\frac{3}{5}$
32. In the following reaction  

$$28\text{NO}_3^- + 3\text{As}_2\text{S}_3 + 4\text{H}_2\text{O} \longrightarrow 6\text{AsO}_4^{3-} + 28\text{NO} + 9\text{SO}_4^{2-} + 8\text{H}^+$$
 equivalent weight of  $\text{As}_2\text{S}_3$  (with molecular weight  $M$ ) is  
 (a)  $\frac{M}{2}$  (b)  $\frac{M}{4}$   
 (c)  $\frac{M}{24}$  (d)  $\frac{M}{28}$
33. In the following reaction :  

$$\text{Cr}(\text{OH})_3 + \text{OH}^- + \text{IO}_3^- \longrightarrow \text{CrO}_4^{2-} + \text{H}_2\text{O} + \text{I}^-$$
 (a)  $\text{IO}_3^-$  is oxidising agent  
 (b)  $\text{Cr}(\text{OH})_3$  is oxidised  
 (c)  $6e^-$  are being taken per I atom  
 (d) All of the above are correct
34. 5.3 g of  $M_2\text{CO}_3$  is dissolved in 150 mL of 1 N HCl. Unused acid required 100 mL of 0.5 N NaOH. Hence, equivalent weight of  $M$  is  
 (a) 23 (b) 12  
 (c) 24 (d) 13
35. Equivalent weight of  $\text{H}_3\text{PO}_2$  when it disproportionates into  $\text{PH}_3$  and  $\text{H}_3\text{PO}_3$  (mol. wt. =  $M$ ) is  
 (a)  $M$  (b)  $\frac{M}{2}$   
 (c)  $\frac{M}{4}$  (d)  $\frac{3M}{4}$
36.  $\text{I}_2$  obtained from 0.1 mol of  $\text{CuSO}_4$  required 100 mL of 1 M hypo solution, hence, mol percentage of pure  $\text{CuSO}_4$  is

- (a) 100 (b) 50  
(c) 25 (d) 40
37. 1.2 g of Mg is treated with 100 mL of 1 M  $\text{H}_2\text{SO}_4$ . Molar concentration of the  $\text{H}_2\text{SO}_4$  solution after complete reaction is  
(a) 0.5 M (b) 0.005 M  
(c) 0.10 M (d) 0.20 M
38. Hardness in water is expressed in terms of ppm of  $\text{CaCO}_3$ . If hardness is 200 ppm  $\text{CaCO}_3$ , then in terms of molarity it is  
(a) 0.004 M (b) 0.002 M  
(c) 0.001 M (d) 0.0005 M
39. 10 mL of a blood sample (containing calcium oxalate) is dissolved in acid. It required 20 mL of 0.001 M  $\text{KMnO}_4$  (which oxidises oxalate to carbon dioxide) hence,  $\text{Ca}^{2+}$  ion in 10 mL blood is  
(a) 0.200 g (b) 0.02 g  
(c) 2.00 g (d) 0.002 g
40. Volume of 18.0 M  $\text{H}_2\text{SO}_4$  required to prepare 1.0 L of a 0.9 M solution of  $\text{H}_2\text{SO}_4$  is  
(a) 50.0 mL (b) 10.0 mL  
(c) 500.0 mL (d) 5.0 mL
41. Volume of 0.50 M NaOH solution required to react with 40.0 mL of 0.05 M  $\text{H}_2\text{SO}_4$  solution is  
(a) 40.0 mL (b) 80.0 mL  
(c) 20.0 mL (d) 8.0 mL
42. Stock phosphoric acid solution is 85%  $\text{H}_3\text{PO}_4$  and has a specific gravity of 1.70. Hence, molarity of  $\text{H}_3\text{PO}_4$  solution is  
(a) 8.51 M (b) 1.70 M  
(c) 14.74 M (d) 7.37 M
43. 150 mL of 6.00 M  $\text{H}_2\text{SO}_4$  solution is mixed with 250 mL of 3.00 M  $\text{H}_2\text{SO}_4$ . Resulting molarity is  
(a) 4.125 M (b) 8.250 M  
(c) 4.500 M (d) 1.650 M
44. If 100 mL of 1.00 M  $\text{H}_2\text{SO}_4$  is mixed with 200 mL of 1.00 M KOH solution, molarity of the salt formed is  
(a) 0.100 M (b) 0.200 M  
(c) 0.333 M (d) 0.666 M
45. Commercial "11.2 volume"  $\text{H}_2\text{O}_2$  solution has a molarity of  
(a) 1 (b) 0.5  
(c) 11.2 (d) 1.12
46. Equivalent weight of  $\text{Cr}_2\text{O}_7^{2-}$  (mol. wt. =  $M$ ) in the following reaction is  

$$\text{Cr}_2\text{O}_7^{2-} + 6\text{I}^- + 14\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 3\text{I}_2 + 7\text{H}_2\text{O}$$
 (a)  $\frac{M}{6}$  (b)  $\frac{M}{3}$   
 (c)  $\frac{M}{2}$  (d)  $M$
47. 0.116 g of  $\text{C}_4\text{H}_4\text{O}_4$  (A) is neutralised by 0.074 g of  $\text{Ca}(\text{OH})_2$ . Hence, protonic hydrogen ( $\text{H}^+$ ) in (A) will be  
(a) 1 (b) 2  
(c) 3 (d) 4
48. 10 mL of  $\text{NaHC}_2\text{O}_4$  is oxidised by 10 mL of 0.02 M  $\text{MnO}_4^-$ . Hence, 10 mL of  $\text{NaHC}_2\text{O}_4$  is neutralised by  
(a) 10 mL of 0.1 M NaOH  
(b) 10 mL of 0.02 M NaOH  
(c) 10 mL of 0.1 M  $\text{Ca}(\text{OH})_2$   
(d) 10 mL of 0.05 N  $\text{Ba}(\text{OH})_2$
49. Oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) forms two series of salt  $\text{HC}_2\text{O}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$ . If 0.9 g of oxalic acid is in 100 mL solution,  $\text{HC}_2\text{O}_4^{2-}$  and  $\text{C}_2\text{O}_4^{2-}$  have normality respectively  
(a) 0.1 N, 0.1 N (b) 0.1 N, 0.2 N  
(c) 0.2 N, 0.2 N (d) 0.2 N, 0.1 N
50. At a given condition, 1 mol  $\text{O}_2$  occupies 30 L. Volume occupied by 1 equivalent of  $\text{O}_2$  is  
(a) 7.5 L (b) 15 L  
(c) 30.0 L (d) 22.4 L
51. 10 g of  $\text{MnO}_2$  on reaction with conc. HCl liberated 0.1 equivalent of  $\text{Cl}_2$  ( $\text{Mn} = 55$ ). Hence, per cent purity of  $\text{MnO}_2$  is  
(a) 87.0 (b) 21.75  
(c) 50.0 (d) 43.5
52. The equivalent mass of a metal is double that of oxygen. How many times is the equivalent mass of its oxide greater than the mass of the metal?  
(a) 2 times (b) 1.5 times  
(c) 3 times (d) 0.5 time
53. 0.106 g of  $\text{Na}_2\text{CO}_3$  completely neutralises 40.0 mL of  $\text{H}_2\text{SO}_4$ . Hence, normality of  $\text{H}_2\text{SO}_4$  solution is  
(a) 0.05 N (b) 0.025 N  
(c) 0.10 N (d) 0.20 N
54. Volume of 0.02 M  $\text{MnO}_4^-$  solution required to oxidise 40.0 mL of 0.1 M  $\text{Fe}^{2+}$  solution is  
(a) 200 mL (b) 100 mL  
(c) 40 mL (d) 20 mL
55. A 20.0 mL solution of  $\text{Na}_2\text{SO}_3$  required 30 mL of 0.01 M  $\text{K}_2\text{Cr}_2\text{O}_7$  solution for the oxidation to  $\text{Na}_2\text{SO}_4$ . Hence, molarity of  $\text{Na}_2\text{SO}_3$  solution is  
(a) 0.015 M (b) 0.045 M  
(c) 0.030 M (d) 0.0225 M
56. Normality of a solution that contains 12.64 g of  $\text{KMnO}_4$  is 500 mL of solution to be used in the reaction that produces  $\text{K}_2\text{MnO}_4$  ion as the reducing product is:  
(a) 0.16 N (b) 0.32 N  
(c) 0.80 N (d) 0.08 N

57. Iodate ion,  $\text{IO}_3^-$ , oxidises  $\text{SO}_3^{2-}$  to  $\text{SO}_4^{2-}$  in acidic medium. If 100 mL sample of solution containing 2.14 g of  $\text{KIO}_3$  reacts with 60 mL of 0.5 M  $\text{Na}_2\text{SO}_3$  solution, then final oxidation state of iodine is  
 (a) +5 (b) +3  
 (c) +1 (d) -1

58. A 0.60 g nitrogen containing compound was boiled with NaOH and  $\text{NH}_3$ , thus formed required 100 mL of 0.2  $\text{NH}_2\text{SO}_4$  for neutralisation; percentage of nitrogen in the compound is  
 (a) 46.67% (b) 23.34%  
 (c) 60.00% (d) 20.00%

59. 1.00 L of 0.15 NaOH absorbed 11.2 millimol of  $\text{CO}_2$  from air. Hence, new molarity of NaOH is  
 (a) 0.1276 M (b) 0.1500 M  
 (c) 0.0224 M (d) 0.0112 M

60. Molarity of  $\text{Na}_2\text{CO}_3$  solution formed in the above question will be  
 (a) 0.0244 M (b) 0.0112 M  
 (c) 0.1500 M (d) 0.1276 M

61. A sample of iron ore weighing 0.740 g containing 24%  $\text{Fe}_2\text{O}_3$  is dissolved and the iron reduced to  $\text{Fe}^{2+}$  by the addition of 25.0 mL of 0.05 M  $\text{SnCl}_2$ . The excess  $\text{Sn}^{2+}$  is oxidised to  $\text{Sn}^{4+}$  using 0.05 M  $\text{HgCl}_2$ . Volume of  $\text{HgCl}_2$  used is  
 (a) 5.2 mL (b) 6.2 mL  
 (c) 5.6 mL (d) 2.6 mL

62. A sample containing only  $\text{Na}_2\text{C}_2\text{O}_4$  and  $\text{KHC}_2\text{O}_4$  required three times the volume of 0.1 N  $\text{KMnO}_4$  for titration as of 0.1 N base (same size sample in each case). Percentage of  $\text{KHC}_2\text{O}_4$  in the mixture is  
 (a) 65.64% (b) 34.36%  
 (c) 30.28% (d) 69.72%

63. A 0.6234 g sample that might contain NaOH,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$  or a mixture of NaOH +  $\text{Na}_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$  +  $\text{NaHCO}_3$  is titrated with 0.1062 M HCl by two-indicator method. It is found that 40.38 mL of the acid is required to reach the phenolphthalein end-point. Methyl orange is then added to the solution, and the titration continued using an additional 12.83 mL of the acid. Thus, sample contained  
 (a) NaOH +  $\text{Na}_2\text{CO}_3$  +  $\text{NaHCO}_3$   
 (b) NaOH +  $\text{Na}_2\text{CO}_3$   
 (c)  $\text{Na}_2\text{CO}_3$  +  $\text{NaHCO}_3$   
 (d) can't be predicted

64. Percentage of NaOH in the mixture of the above example is  
 (a) 18.77% (b) 23.17%  
 (c) 37.54% (d) 46.34%

65. A bottle which contains 200 mL of 0.100 M NaOH absorbs 1.00 mmol of  $\text{CO}_2$  from the air. If the solution

is then titrated with standard acid using phenolphthalein indicator, what normality of the acid will be found?

- (a) 0.190 N (b) 0.380 N  
 (c) 0.095 N (d) 0.0475 N

### One or More Than One Options Correct

- 1 g equivalent of a substance is the weight of that amount of a substance which is equivalent to  
 (a) 0.25 mol  $\text{O}_2$  (b) 8 g  $\text{O}_2$   
 (c) 16 g  $\text{O}_2$  (d) 0.50 mol  $\text{O}_2$
- 2.84 g of  $\text{P}_4\text{O}_{10}$  is dissolved in 1 L aqueous solution. Thus,  
 (a) resulting solution is 0.01 M  
 (b) it is neutralised to  $\text{Na}_3\text{PO}_4$  by 400 mL of 0.3 M NaOH solution  
 (c) it is neutralised to  $\text{CaHPO}_4$  by 400 mL of 0.1 M  $\text{Ca}(\text{OH})_2$  solution  
 (d) it cannot be neutralised by basic solution
- A solution of  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  is 0.2 N as an acid. Then it is  
 (a) 0.267 N as reducing agent  
 (b) 0.6 M as an acid  
 (c) 0.067 M as an acid  
 (d) 0.067 M as reducing agent
- A sample of water has a hardness expressed as 77.5 ppm  $\text{Ca}^{2+}$ . This sample is passed through an ion exchange column and the  $\text{Ca}^{2+}$  is replaced by  $\text{H}^+$ . Select correct statement(s).  
 (a) pH of the water after it has been so treated is 2.4  
 (b) Every  $\text{Ca}^{2+}$  ion is replaced by one  $\text{H}^+$  ion  
 (c) Every  $\text{Ca}^{2+}$  ion is replaced by two  $\text{H}^+$  ions  
 (d) pH of the solution remains unchanged
- 10.78 g of  $\text{H}_3\text{PO}_4$  in 550 mL solution is 0.40 N. Thus, this acid  
 (a) has been neutralised to  $\text{HPO}_4^{2-}$   
 (b) has been neutralised to  $\text{PO}_4^{3-}$   
 (c) has been reduced to  $\text{HPO}_3^{2-}$   
 (d) has been neutralised to  $\text{H}_2\text{PO}_4^-$
- Mass of  $\text{KHC}_2\text{O}_4$  (potassium acid oxalate) required to reduce 100 mL of 0.02 M  $\text{KMnO}_4$  in acidic medium (to  $\text{Mn}^{2+}$ ) is  $x$  g and to neutralise 100 mL of 0.05 M  $\text{Ca}(\text{OH})_2$  is  $y$  g, then  
 (a)  $x = y$  (b)  $2x = y$   
 (c)  $x = 2y$  (d) None of these
- A mixture of  $\text{Na}_2\text{C}_2\text{O}_4$  (A) and  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$  (B) required equal volumes of 0.1 M  $\text{KMnO}_4$  and 0.1 M NaOH separately. Molar ratio of A and B in the mixture is  
 (a) 1:1 (b) 1:5.5  
 (c) 5.5:1 (d) 3.1:1

8.  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{NaHC}_2\text{O}_4$  behave as acids as well as reducing agents. Which are correct statements?
  - (a) Equivalent weight of  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{NaHC}_2\text{O}_4$  are equal to their molecular weights when behaving as reducing agents
  - (b) 100 mL of 1 M solution of each is neutralised by equal volumes of 1 M  $\text{Ca}(\text{OH})_2$
  - (c) 100 mL of 1 N solution of each is neutralised by equal volumes of 1 N  $\text{Ca}(\text{OH})_2$
  - (d) 100 mL of 1 M solution of each is oxidised by equal volumes of 1 M  $\text{KMnO}_4$
9. 100 mL of 1.44% solution of pure  $\text{FeC}_2\text{O}_4$  in dil. HCl is oxidised by 0.01 M  $\text{KMnO}_4$ . Then volume of  $\text{KMnO}_4$  required is
  - (a) 120 mL
  - (b) 600 mL
  - (c) 200 mL
  - (d) 60 mL
10. 1 mole of  $\text{MnO}_4^{2-}$  in neutral aqueous solution disproportionates to
  - (a)  $\frac{2}{3}$  mol of  $\text{MnO}_4^-$  and  $\frac{1}{3}$  mol of  $\text{MnO}_2$
  - (b)  $\frac{1}{3}$  mol of  $\text{MnO}_4^-$  and  $\frac{2}{3}$  mol of  $\text{MnO}_2$
  - (c)  $\frac{1}{3}$  mol of  $\text{Mn}_2\text{O}_7$  and  $\frac{1}{3}$  mol of  $\text{MnO}_2$
  - (d)  $\frac{2}{3}$  mol of  $\text{Mn}_2\text{O}_7$  and  $\frac{1}{3}$  mol of  $\text{MnO}_2$
4. We define  $p$ -value of a term (say  $x$ ) as
 
$$p_x = -\log x$$
 Calculate  $p$ -value for each ion in a solution that is  $2.00 \times 10^{-3}$  M in  $\text{NaCl}$  and  $5.4 \times 10^{-4}$  M  $\text{HCl}$ .
5. Calculate molar concentration of  $\text{Ag}^+$  in a solution that has  $p_{\text{Ag}} = 6.6990$
6. What mass of  $\text{Ag}_2\text{CO}_3$  is formed when 25.0 mL of 0.2 M  $\text{AgNO}_3$  is mixed with 50.0 mL of 0.08 M  $\text{Na}_2\text{CO}_3$ ?
7. What is the molar concentration of  $\text{Na}_2\text{CO}_3$  in the solution when 25.0 mL of 0.2 M  $\text{AgNO}_3$  are mixed with 50.0 mL of 0.08 M  $\text{Na}_2\text{CO}_3$  solution?
8. Calculate the  $p$ -value for each of the indicated ions in the following
  - (a)  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{NO}_3^-$  in a solution that is  $4.78 \times 10^{-2}$  M in  $\text{Cu}(\text{NO}_3)_2$  and 0.104 M in  $\text{Zn}(\text{NO}_3)_2$ .
  - (b)  $\text{H}^+$ ,  $\text{Ba}^{2+}$  and  $\text{ClO}_4^-$  in a solution that is  $3.35 \times 10^{-4}$  M in  $\text{Ba}(\text{ClO}_4)_4$  and  $6.75 \times 10^{-4}$  M in  $\text{HClO}_4$ .
9. Sea water contains an average of  $1.08 \times 10^3$  ppm of  $\text{Na}^+$  and 270 ppm of  $\text{SO}_4^{2-}$ . Calculate
  - (a) the molar concentration of  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  given that average density of sea water is 1.02 g/mL
  - (b) the  $p_{\text{Na}}$  and  $p_{\text{SO}_4^{2-}}$  for sea water
10. A solution was prepared by dissolving 5.76 g of  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  in sufficient water to give 2.00 L. Calculate.
  - (a) the molar analytical concentration of  $\text{KCl} \cdot \text{MgCl}_2$
  - (b) the molar concentration of  $\text{Mg}^{2+}$  and  $\text{Cl}^-$
  - (c) the number of millimoles of  $\text{Cl}^-$  in 25.0 mL of this solution
  - (d) ppm  $\text{K}^+$

## Brain Twisters

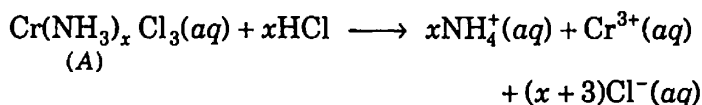
1. You place 2.56 g  $\text{CaCO}_3$  (calcium carbonate) in a beaker containing 250 mL of 0.125 M  $\text{HCl}$ . When the reaction has ceased, does any  $\text{CaCO}_3$  remain? What mass of  $\text{CaCl}_2$  can be produced?
 
$$\text{CaCO}_3(s) + 2\text{HCl}(aq) \longrightarrow \text{CaCl}_2(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l)$$
2. Gold can be dissolved from gold-bearing rock by treating the rock with sodium cyanide ( $\text{NaCN}$ ) in the presence of oxygen.
 
$$4\text{Au}(s) + 8\text{NaCN}(aq) + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \longrightarrow 4\text{NaAu}(\text{CN})_2(aq) + 4\text{NaOH}(aq)$$
  - (a) Name the oxidising and reducing agents in this reaction. What has been oxidised and what has been reduced?
  - (b) If you have exactly one metric ton (1 metric ton = 1000 kg) of gold-bearing rock, what volume of 0.075 M  $\text{NaCN}$ , in litres, do you need to extract the gold if the rock is 0.0197% gold? ( $\text{Au} = 197$ )
3. 500 mL of 0.25 M  $\text{Na}_2\text{SO}_4$  solution is added to an aqueous solution of 15.00 g of  $\text{BaCl}_2$  solution resulting in the formation of white precipitate of  $\text{BaSO}_4$ . Which is the limiting reactant? Calculate moles of  $\text{BaSO}_4$  formed. ( $\text{Ba} = 137, \text{S} = 32, \text{O} = 16, \text{Na} = 23$ )
4. The phosphorus in a 4.258 g sample of a plant food was converted to  $\text{PO}_4^{3-}$  and precipitated as  $\text{Ag}_3\text{PO}_4$  through the addition of 50.0 mL of 0.082 M  $\text{AgNO}_3$ . The excess of  $\text{AgNO}_3$  was back-titrated with 4.86 mL of 0.0625 M  $\text{KSCN}$ . Express the results of this analysis in terms of  $\text{P}_2\text{O}_5$ .
 
$$\begin{aligned} \text{P}_2\text{O}_5 + 9\text{H}_2\text{O} &\longrightarrow 2\text{PO}_4^{3-} + 6\text{H}_3\text{O}^+ \\ 2\text{PO}_4^{3-} + 6\text{Ag}^+ &\longrightarrow 2\text{Ag}_3\text{PO}_4(s) \\ \text{Ag}^+ + \text{SCN}^- &\longrightarrow \text{AgSCN}(s) \end{aligned}$$

14. How many mL of 0.30 M  $\text{CaCl}_2$  must be added to 400 mL of 0.20 M  $\text{KCl}$  to produce a solution of 0.25 M  $\text{Cl}^-$ ?
15. How many kg of wet  $\text{NaOH}$  containing 12% water is required to prepare 60 L of 0.50 M  $\text{NaOH}$  solution?
16. Exactly 50.0 mL of  $\text{Na}_2\text{CO}_3$  solution is equivalent to 56.3 mL of 0.102 N  $\text{HCl}$  in acid-base neutralisation. How many gram  $\text{CaCO}_3$  would be precipitated if an excess of  $\text{CaCl}_2$  solution were added to 100 mL of this  $\text{Na}_2\text{CO}_3$  solution?
17. What mass of phosphoric acid,  $\text{H}_3\text{PO}_4$  is required to prepare 550 mL of 0.40 N solution?  
 (a) assuming complete neutralisation of acid  
 (b) assuming reduction to  $\text{HPO}_3^{2-}$
- $$\text{H}_3\text{PO}_4 + 3\text{OH}^- \longrightarrow 3\text{H}_2\text{O} + \text{PO}_4^{3-}$$
- $$\text{H}_3\text{PO}_4 + 2e^- \longrightarrow \text{HPO}_3^{2-} + \text{H}_2\text{O}$$
18. The tetraethyl lead, TEL,  $[\text{Pb}(\text{C}_2\text{H}_5)_4]$  in a 25.00 mL sample of aviation gasoline was shaken with 15.00 mL of 0.02095 M  $\text{I}_2$
- $$\text{Pb}(\text{C}_2\text{H}_5)_4 + \text{I}_2 \longrightarrow \text{Pb}(\text{C}_2\text{H}_5)_3\text{I} + \text{C}_2\text{H}_5\text{I}$$
- After the reaction, unused  $\text{I}_2$  required 6.09 mL of 0.03465 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Calculate molar concentration of TEL.

## Passage Comprehension Questions

### Passage 1

Chromium (III) ion forms many compounds with ammonia. To find the formula of one of these compounds, you titrate the  $\text{NH}_3$  in the compound with standardised acid



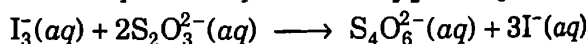
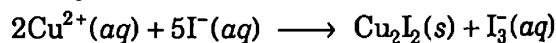
Assume that 40 mL of 1.5 M  $\text{HCl}$  is used to titrate 2.635 g of (A).

Based on the above experiment, answer the following questions.

- Value of  $x$  is  
 (a) 3 (b) 4  
 (c) 5 (d) 6
- If 1.5 M  $\text{H}_2\text{SO}_4$  is used instead of 1.5 M  $\text{HCl}$ , titre value is  
 (a) 40 mL (b) 20 mL  
 (c) 10 mL (d) 15 mL
- Probable complex (assume that coordination number of chromium is six) can be  
 (a)  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$   
 (b)  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$   
 (c)  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$   
 (d)  $[\text{CrCl}_3] \cdot 6\text{NH}_3$

### Passage 2

Copper containing alloy weighing 0.3175 g is dissolved in an acid, and an excess of  $\text{KI}$  is added. Estimation of copper in alloy is based on following reaction



Answer the following questions based on the above reaction.

- Oxidising agent (O) and reducing agent (R) in the above reaction :  

| O                                               | R                                         |
|-------------------------------------------------|-------------------------------------------|
| (a) $\text{Cu}^{2+}, \text{S}_2\text{O}_3^{2-}$ | $\text{I}_3^-, \text{I}^-$                |
| (b) $\text{Cu}^{2+}, \text{S}_2\text{O}_3^{2-}$ | $\text{I}_3^-$                            |
| (c) $\text{Cu}^{2+}, \text{I}_3^-$              | $\text{I}^-, \text{S}_2\text{O}_3^{2-}$   |
| (d) $\text{Cu}^{2+}, \text{I}^-$                | $\text{I}_3^-, \text{S}_2\text{O}_3^{2-}$ |
- Estimation is based on  
 (a) iodometry (b) iodimetry  
 (c) gravimetry (d) colorimetry
- If 25 mL of 0.10 M  $\text{Na}_2\text{S}_2\text{O}_3$  is required, Cu present in alloy is  
 (a) 20% (b) 40%  
 (c) 45% (d) 50%
- $\text{I}_2$  formed is converted to  $\text{KI}_3$  in the given reaction. This shows  
 (a)  $\text{I}_2$  is soluble in  $\text{H}_2\text{O}$  (b)  $\text{I}_2$  is a Lewis acid  
 (c)  $\text{I}_2$  is ionic compound (d)  $\text{I}^-$  is a Lewis base

### Passage 3

Consider the titration of solution X of 1 M  $\text{HCl}$  using 0.1 M  $\text{NaOH}$  solution with phenolphthalein indicator, by two students A and B.

| Student | Process                                                                  | Titre volume of $\text{NaOH}$ |
|---------|--------------------------------------------------------------------------|-------------------------------|
| A       | 20 mL $\text{HCl}$ + 20 mL $\text{H}_2\text{O}$ + 1 drop phenolphthalein | $V_A$                         |
| B       | 20 mL $\text{HCl}$ + 60 mL $\text{H}_2\text{O}$ + 1 drop phenolphthalein | $V_B$                         |

Answer the following questions

- What is the relation between  $V_A$  and  $V_B$ ?  
 (a)  $V_A = V_B$  (b)  $2V_A = V_B$   
 (c)  $V_A = 2V_B$  (d)  $3V_A = V_B$
- Before titration, resultant molarity of  $\text{HCl}$  of the student A after addition of  $\text{H}_2\text{O}$  is  
 (a) same as that of B (b) double as that of B  
 (c) half as that of B (d) one third as that of B
- End-point is  
 (a) appearance of blue colour  
 (b) disappearance of blue colour  
 (c) appearance of pink colour  
 (d) disappearance of blue colour

### Passage 4

For titrating a certain volume of a reducing substance by 1 M  $\text{KMnO}_4$ , it is found that 20 mL was used in acidic medium, 33.4 mL was used in alkaline medium and 100 mL was used in neutral medium.  $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$  in acidic medium.

Based on this study, answer the following questions.

- To what state  $\text{MnO}_4^-$  is reduced to in alkaline medium?  
(a) +4 (b) +1  
(c) +5 (d) +6
- To what state  $\text{MnO}_4^-$  is reduced to in neutral medium?  
(a) +4 (b) +5  
(c) +6 (d) +7
- 1 M  $\text{KMnO}_4$  expressed in terms of normality is in

|     | Acidic medium | Alkaline medium | Neutral medium |
|-----|---------------|-----------------|----------------|
| (a) | 1 N           | 1 N             | 1 N            |
| (b) | 5 N           | 3 N             | 1 N            |
| (c) | 1 N           | 3 N             | 5 N            |
| (d) | 0.2 N         | 0.33 N          | 1 N            |

### Passage 5

Both  $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$  and  $\text{MnO}_4^-(\text{aq})$  can be used to titrate  $\text{Fe}^{2+}(\text{aq})$ . You have been provided with 0.1 M solution of each and volumetric estimation is carried in acidic medium. Suppose for the given volume of  $\text{Fe}^{2+}$  solution :

$$V_1 = \text{volume of } \text{MnO}_4^-$$

$$V_2 = \text{volume of } \text{Cr}_2\text{O}_7^{2-}$$

required in the oxidation to  $\text{Fe}^{3+}$ .

Based on this experimental study, answer the following questions :

- Select correct alternate.  
1  $\text{Fe}^{2+}$  is equivalent to  
(a)  $\frac{1}{5}$  mol of  $\text{MnO}_4^-$   
(b)  $\frac{1}{6}$  mol of  $\text{Cr}_2\text{O}_7^{2-}$   
(c) 1 equivalent each of  $\text{MnO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$   
(d) All of the above
- (a)  $V_1 = V_2$   
(b)  $V_1 > V_2$   
(c)  $V_1 < V_2$   
(d) nothing can be predicted
- 24.50 mL of 0.1 M  $\text{Cr}_2\text{O}_7^{2-}$  is required in the oxidation of given volume of 0.1 M  $\text{Fe}^{2+}$ . 0.1 M  $\text{MnO}_4^-$  required will be  
(a) 29.40 mL (b) 24.50 mL  
(c) 20.42 mL (d) 20.10 mL

### Passage 6

Following experiment is designed to determine calcium content in the blood. Read the experiment and answer the questions at the end of it.

Calcium oxalate ( $\text{CaC}_2\text{O}_4$ ) is insoluble in water. For this reason it can be used to determine the amount of  $\text{Ca}^{2+}$  ions in fluids such as blood. The calcium oxalate isolated from blood is dissolved in acid and titrated against a standardized  $\text{KMnO}_4$  solution.

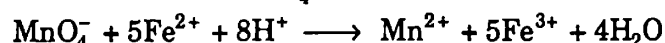
Answer the following questions

- In one test it is found that the calcium oxalate isolated from a 10.0 mL sample of blood requires 25 mL of  $1 \times 10^{-3}$  M  $\text{KMnO}_4$  for titration. Calculate the number of milligrams of calcium per mL of blood  
(a) 0.50 (b) 10.0  
(c) 0.25 (d) 5.0
- Milliequivalents of  $\text{KMnO}_4$  used were  
(a) 0.125 (b) 0.025  
(c) 0.250 (d) 0.050
- Calcium content expressed in ppm is  
(a) 250 (b) 200  
(c) 150 (d) 100
- Above titration takes place in acidic medium. Acid chosen is  
(a)  $\text{H}_2\text{SO}_4$  (b)  $\text{HCl}$   
(c)  $\text{CH}_3\text{COOH}$  (d)  $\text{HCOOH}$
- Indicator in the above titration is  
(a) phenolphthalein  
(b) methylene blue  
(c) methyl orange  
(d)  $\text{KMnO}_4$  (self-indicator)

### Passage 7

Following titration method is given to determine total content of the species with variable oxidation states. Answer the questions given at the end of it.

A quantity of 25.0 mL of solution containing both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions is titrated with 25.0 mL of 0.0200 M  $\text{KMnO}_4$  (in dilute  $\text{H}_2\text{SO}_4$ ). As a result, all of the  $\text{Fe}^{2+}$  ions are oxidised to  $\text{Fe}^{3+}$  ions. Next 25 mL of the original solution is treated with Zn metal. Finally, the solution requires 40.0 mL of the same  $\text{KMnO}_4$  solution for oxidation to  $\text{Fe}^{3+}$ .



Answer the following questions

- Molar concentration of  $\text{Fe}^{2+}$  in the original solution is  
(a) 0.01 M (b) 0.02 M  
(c) 0.10 M (d) 0.20 M
- Molar concentration of  $\text{Fe}^{3+}$  in the original solution is  
(a) 0.06 M (b) 0.16 M  
(c) 0.032 M (d) 0.012 M
- Zinc added in the second titration will  
(a) oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  (b) reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$   
(c) reduce  $\text{Fe}^{3+}$  to Fe (d) reduce  $\text{Fe}^{2+}$  to Fe

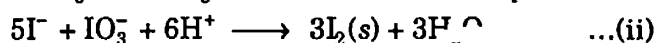
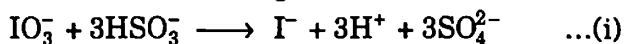


4. If 0.02 M  $K_2Cr_2O_7$  is used instead of 0.02 M  $KMnO_4$ , its volume required in these titrations are respectively
- (a) 25 mL, 40 mL                      (b) 25 mL, 15 mL  
(c) 20.8 mL, 33.3 mL                (d) 10.4 mL, 16.7 mL

### Passage 8

Following short write-up describes synthesis of  $I_2$  from natural source chile saltpetre. Answer the questions at the end of it.

Chile saltpetre is a natural source of  $NaIO_3$  which also contains  $NaIO_3$ . The  $NaIO_3$  can be used as a source of iodine produced in the following reactions:



1.00 L of the starting solution which contains 5.80 g  $NaIO_3$  / L, is treated with stoichiometric quantity of  $NaHSO_3$ . Then a further quantity of the starting solution is added to the reaction mixture to bring about the second reaction. [I = 127, Na = 23, S = 32]

Answer the following questions

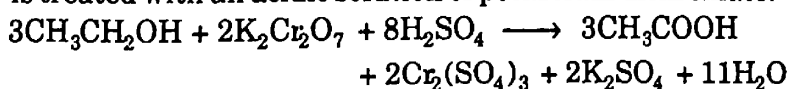
- How many grams of  $NaHSO_3$  are required in step (i)?  
(a) 5.80 g                                      (b) 17.4 g  
(c) 9.14 g                                      (d) 3.0 g
- What additional volume of the starting solution must be added in step (ii)?  
(a) 0.2 L                                      (b) 0.4 L  
(c) 0.8 L                                      (d) 1.0 L
- How many equivalents of  $IO_3^-$  are present in one mole of  $NaIO_3$  in step (i)?  
(a) 2                                              (b) 4  
(c) 6                                              (d) 8
- How many equivalents of  $IO_3^-$  are used in step (ii)?  
(a) 6                                              (b) 5  
(c) 0.06                                        (d) 0.035

### Passage 9

Following passage is for the drunken drivers on roads which are becoming fatal by their wrong driving.

Every year in our country about 25,000 people are killed and 500,000 more are injured as a result of drunk driving. In spite of efforts to educate the public about the dangers of driving while intoxicated and stiffer penalties for drunk driving offenses, law enforcement agencies still have to devote a great deal of work to remove drunk drivers from roads.

The police often use a device called a breath analyser to test drivers suspected to being drunk. The chemical basis of this device is a redox reaction. A sample of the driver's breath is drawn into the breath analyser, where it is treated with an acidic solution of potassium dichromate.



The driver's blood alcohol level can be determined readily by measuring the degree of this colour change (read from a calibrated meter on the instrument). The current legal limit of blood alcohol content is 0.1 per cent by mass. Anything higher constitutes intoxication.

Read the passage and answer the questions given below

- Above test is based on  
(a) smell of ethanol and ethanoic acid  
(b) change of colour yellow to blue  
(c) change of colour orange to green  
(d) change of colour orange to colourless
- Equivalent mass of  $K_2Cr_2O_7$  is  
(a)  $\frac{\text{molar mass}}{6}$                                       (b)  $\frac{\text{molar mass}}{3}$   
(c)  $\frac{\text{molar mass}}{2}$                                       (d)  $\frac{\text{molar mass}}{1}$
- Equivalent mass of  $CH_3CH_2OH$  is  
(a)  $\frac{\text{molar mass}}{1}$                                       (b)  $\frac{\text{molar mass}}{2}$   
(c)  $\frac{\text{molar mass}}{3}$                                       (d)  $\frac{\text{molar mass}}{4}$
- The alcohol content in a 10.0 g sample of blood from a driver required 4.23 mL of 0.07654 M  $K_2Cr_2O_7$  for titration. Should the police prosecute the individual for drunken driving?  
(a) Yes                                              (b) No  
(c) Nothing can be predicted

### Assertion & Reason

Codes :

- (a) Both A and R are true and R is the correct explanation of A.  
(b) Both A and R are true but R is not the correct explanation of A.  
(c) A is true but R is false.  
(d) A is false but R is true.

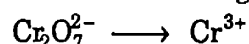
1. **Assertion (A)** : If a solution is 20% by weight of solute, then it is 25% by weight of solvent.

**Reason (R)** : Solution also includes weight of solvent and thus, pure solvent is 80 g which contains 20 g solute.

2. **Assertion (A)** : Molality is independent of temperature.

**Reason (R)** : Volume of solution does not change with temperature.

3. **Assertion (A)** : In the following half reaction:



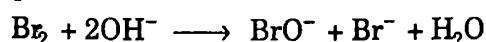
$$\text{Equivalent weight of } Cr_2O_7^{2-} = \frac{\text{Molar mass}}{3}$$

**Reason (R)** : Change in oxidation number of chromium is 3 per atom.

4. **Assertion (A)** : 1.575 g  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  in 250 mL solution makes it 0.1 N.

**Reason (R)** :  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  is a dihydrate organic acid.

5. **Assertion (A)** : Following reaction is a disproportionation reaction:



**Reason (R)** :  $\text{Br}_2$  is oxidised to  $\text{BrO}^-$  as well as reduced to  $\text{Br}^-$ .

## True & False

1. A solution 20% by mass of solvent is 25% by mass of solution.
2. Equivalent mass of  $\text{Cr}_2\text{O}_7^{2-}$  in the following reaction is M/6.



3. 100 mL of 1 M  $\text{SO}_2\text{Cl}_2$  aqueous solution is neutralised by 100 mL of 4 N NaOH.
4.  $\text{H}_2\text{O}_2$  can be estimated by  $\text{MnO}_4^-$  in acidic as well as in basic medium.
5. Iodimetric estimation includes  $\text{CuSO}_4$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{MnO}_4^-$ ,  $\text{CaOCl}_2$ ,  $\text{MnO}_2/\text{HCl}$  which on treatment with KI liberate  $\text{I}_2$ .
6. In iodometric titration of  $\text{Cr}_2\text{O}_7^{2-}$ , there is bluish green colour at the end point.
7. Concentration of 1 ppm means that 1 L solution contains 1 mg solute.
8. "10 volume  $\text{H}_2\text{O}_2$ " means 1 mL of  $\text{H}_2\text{O}_2$  concentrated solution has been diluted to 10 mL.
9. "1 volume  $\text{H}_2\text{O}_2$ " solution means that 1 mL of  $\text{H}_2\text{O}_2$  at NTP gives 1 L of  $\text{O}_2$ .
10. Ferric sulphate is oxidised by  $\text{MnO}_4^-/\text{H}^+$ .
11. In the titration of  $\text{Fe}^{2+}$  with  $\text{MnO}_4^-$ ,  $\text{MnO}_4^-$  is self-indicator.
12. Concentration of  $\text{H}_2\text{C}_2\text{O}_4$  can be determined by  $\text{MnO}_4^-/\text{H}^+$  as well as by NaOH.
13. Only 50% of  $\text{Na}_2\text{CO}_3$  solution is indicated if it is neutralised by HCl using phenolphthalein as the indicator.
14. Estimation of nitrogen is done by Kjeldahl method.
15.  $\text{SO}_2$  turns acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution to colourless solution.

## Fill in the Blanks

1. If molecular weight of  $\text{KMnO}_4$  is 158, then its equivalent weight is ..... in acidic medium.
2. Equivalent of  $\text{KMnO}_4$  is 158 when it changes to .....

3. Pyrolusite can be estimated by .....

4. Concentration of  $\text{Na}_2\text{CO}_3$  solution can be determined by titration with acid solution using ..... as the indicator.
5. End point in the titration of  $\text{CuSO}_4$  iodometrically (with starch as the indicator) is the .....
6. Concentration of 1 mg per litre is equal to ..... ppm.
7. If 900 mL  $\text{H}_2\text{O}$  is added to 100 mL of 1 M  $\text{H}_2\text{SO}_4$ , then it is ..... N  $\text{H}_2\text{SO}_4$ .
8.  $\text{MnO}_4^-$  oxidises  $\text{Mn}^{2+}$  to  $\text{MnO}_2$  and itself reduces to ..... in the titration method.
9. Normality of the mixture of 100 mL 1 N HCl and 50 mL 2 N  $\text{H}_2\text{SO}_4$  is .....
10. If 100 mL of  $\text{SO}_2$  solution required 50 mL of 0.01 M  $\text{Cr}_2\text{O}_7^{2-}$  in acidic medium then  $\text{SO}_2$  solution is .....
11. Normality of the mixture of 100 mL 1 N HCl and 50 mL 1 N NaOH is ..... and the mixture is .....
12. 100 mL of a mixture of  $\text{FeSO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$  required 50 mL of 0.1 N  $\text{KMnO}_4$  solution, then concentration of  $\text{Fe}^{2+}$  is ..... g  $\text{L}^{-1}$ .
13. Ozone in the atmosphere is determined by .....
14.  $\text{BrO}_3^-$  oxidises  $\text{I}^-$  to ..... and thus equivalent weight of  $\text{BrO}_3^-$  is .....
15.  $\text{I}_2$  oxidises  $\text{N}_2\text{H}_4$  to .....

## Matrix-Match Type Questions

### I. Only One Correct

1. Match the reaction (in List I) with titration method (in List II).

| List I                                                                                                                                                        | List II       |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| A. $\text{N}_2\text{H}_4 + 2\text{I}_2 \longrightarrow \text{N}_2 + 4\text{H}^+ + 4\text{I}^-$                                                                | 1. Iodometric |
| B. $2\text{CuSO}_4 + 4\text{KI} \longrightarrow \text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4 + \text{I}_2$                                                  | 2. Redox      |
| C. $\text{MnO}_4^- + \text{Fe}^{2+} \longrightarrow \text{Mn}^{2+} + \text{Fe}^{3+}$                                                                          | 3. Kjeldahl   |
| D. $\text{NH}_4\text{Cl} + \text{NaOH} \xrightarrow{\Delta} \text{NH}_3$<br>$2\text{NH}_3 + \text{H}_2\text{SO}_4 \longrightarrow (\text{NH}_4)_2\text{SO}_4$ | 4. Iodimetric |

2. Match the half-reaction (in List I) with equivalent mass (molar mass = M) (in List II).

| List I                                                                 | List II |
|------------------------------------------------------------------------|---------|
| A. $\text{Cr}_2\text{O}_7^{2-} \longrightarrow \text{Cr}^{3+}$         | 1. M    |
| B. $\text{C}_2\text{O}_4^{2-} \longrightarrow \text{CO}_2$             | 2. M/2  |
| C. $\text{MnO}_4^- \longrightarrow \text{MnO}_2$                       | 3. M/6  |
| D. $\text{HC}_2\text{O}_4^- \longrightarrow \text{C}_2\text{O}_4^{2-}$ | 4. M/3  |

3. Match the reactants (in List I) with the indicator (in List II).

| List I                                                     | List II                                 |
|------------------------------------------------------------|-----------------------------------------|
| A. $\text{Fe}^{2+} / \text{Cr}_2\text{O}_7^{2-}$           | 1. Ferric alum                          |
| B. $\text{AgNO}_3 / \text{CNS}^-$                          | 2. $\text{MnO}_4^-$ (self)              |
| C. $\text{CuSO}_4 / \text{KI} / \text{S}_2\text{O}_3^{2-}$ | 3. $\text{K}_3[\text{Fe}(\text{CN})_6]$ |
| D. $\text{Fe}^{2+} / \text{MnO}_4^-$                       | 4. Starch                               |

4. Match the reaction (in List I) with the colour at the final stage (in List II).

| List I                                                      | List II               |
|-------------------------------------------------------------|-----------------------|
| A. $\text{MnO}_4^- / \text{H}^+ / \text{Fe}^{2+}$           | 1. Deep reddish brown |
| B. $\text{MnO}_4^- / \text{conc. OH}^- / \text{Mn}^{2+}$    | 2. Colourless         |
| C. $\text{MnO}_4^- / \text{H}_2\text{O} / \text{dil. OH}^-$ | 3. Blackish brown     |
| D. $\text{CuSO}_4 / \text{KI}$                              | 4. Green              |

## II. One or More Correct

1. Match the reactant (in Column I) with the type of titration (in Column II) used for estimation.

| Column I                                                                      | Column II              |
|-------------------------------------------------------------------------------|------------------------|
| A. $\text{KHC}_2\text{O}_4$                                                   | 1. Acid-Base titration |
| B. $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ | 2. Redox titration     |
| C. $\text{CuSO}_4$                                                            | 3. Iodometric          |
| D. $\text{I}_2$                                                               | 4. Iodimetric          |
| E. $\text{K}_2\text{Cr}_2\text{O}_7$                                          |                        |

2. Match the half-reaction (oxidation or reduction) (in Column I) with number of electrons exchanged (in Column II).

| Column I                                                        | Column II |
|-----------------------------------------------------------------|-----------|
| A. $3\text{I}^- \longrightarrow \text{I}_3^-$                   | 1. 5      |
| B. $\text{Cr}_2\text{O}_7^{2-} \longrightarrow 2\text{Cr}^{3+}$ | 2. 6      |
| C. $\text{Cl}^- \longrightarrow \text{ClO}_3^-$                 | 3. 2      |
| D. $\text{N}_2 \longrightarrow \text{N}_2\text{H}_4$            | 4. 4      |
| E. $\text{MnO}_4^- \longrightarrow \text{Mn}^{2+}$              |           |
| F. $\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{CO}_2$     |           |

## Integer Answer Types

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the ORS have to be darkened. For example, if the correct answers to question number X, Y, Z and W (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will like the following :

| X | Y | Z | W |
|---|---|---|---|
| ① | ① | ① | ① |
| ② | ② | ② | ② |
| ③ | ③ | ③ | ③ |
| ④ | ④ | ④ | ④ |
| ⑤ | ⑤ | ⑤ | ⑤ |
| ⑥ | ⑥ | ⑥ | ⑥ |
| ⑦ | ⑦ | ⑦ | ⑦ |
| ⑧ | ⑧ | ⑧ | ⑧ |
| ⑨ | ⑨ | ⑨ | ⑨ |

## Set I

- 1 M  $\text{MnO}_4^-$  solution is  $x$  equiv.  $\text{L}^{-1}$  when reduced to  $\text{Mn}^{2+}$ . Thus,  $x$  is .....
- 1 M  $\text{Cr}_2\text{O}_7^{2-}$  solution is  $y$  equiv.  $\text{L}^{-1}$ . Thus,  $y$  is .....
- 1 M  $\text{C}_2\text{O}_4^{2-}$  solution is  $z$  equiv.  $\text{L}^{-1}$ . Thus,  $z$  is .....
- 6.3 g of an acid (molar mass =  $126 \text{ g mol}^{-1}$ ) reacts completely with 100 mL of 0.5  $\text{Ca}(\text{OH})_2$  solution. Thus basicity of acid is .....
- We want to prepare 2 L of 0.025 M  $\text{CH}_3\text{COOH}$  solution. Amount of  $\text{CH}_3\text{COOH}$  dissolved is .....
- 100 mL of 0.01 M  $\text{XO}_4^-$  is reduced to  $\text{X}^{n+}$  by 100 mL of 0.05 M  $\text{Fe}^{2+}$  in acidic medium. Thus, oxidation state of X in  $\text{X}^{n+}$  is .....
- $\text{Cr}(\text{NH}_3)_x\text{Cl}_3(\text{aq})$  solution is titrated with  $\text{HCl}(\text{aq})$  solution.  

$$\text{Cr}(\text{NH}_3)_x\text{Cl}_3(\text{aq}) + x\text{HCl}(\text{aq}) \longrightarrow x\text{NH}_4^+(\text{aq}) + \text{Cr}^{3+}(\text{aq}) + (x+3)\text{Cl}^-(\text{aq})$$
 Assume that 24.26 mL of 1.5 M  $\text{HCl}$  is used to titrate 1.580 g of  $\text{Cr}(\text{NH}_3)_x\text{Cl}_3$ . Thus,  $x$  is .....
- 250 mL of 0.1 M  $\text{NaOH}$  contains  $x$  g of  $\text{NaOH}$ . Thus,  $x$  is .....

## Set II

1. Basicity of  $\text{H}_3\text{PO}_4$  is .....
2. Basicity of  $\text{H}_3\text{PO}_3$  is .....
3. Basicity of  $\text{H}_3\text{PO}_2$  is .....
4. 2 moles of  $\text{MnO}_4^-$  oxidise ..... moles of  $\text{NaHC}_2\text{O}_4$ .
5. Ionisable H atoms in acetic acid  $\text{C}_2\text{H}_4\text{O}_2$  is .....
6. 20 mL of 1 M  $\text{MnO}_4^-$  are required in acidic medium and 100 mL of 1 M  $\text{MnO}_4^-$  are required in neutral medium in a redox titration. If  $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$  in acidic medium, oxidation number of Mn in reduced species in neutral medium is .....
7. 22.4 L is the volume of ..... equivalent(s) of  $\text{O}_2$  gas at NTP.
8. 25 mL of 0.1 M solution of metallic salt (A) oxidises 25 mL of 0.1 M sodium sulphite to sodium sulphate. If oxidation number of the metal in the salt (A) is 3, then new oxidation number of the metal is .....

## Set III

1. Complex  $\text{Cr}(\text{NH}_3)_x\text{Cl}_3$  (A) is titrated with 1.5 M HCl. 40 mL of HCl are required to titrate 2.635 g of A. Thus,  $x$  is .....
2. Mixture containing 1 mole  $\text{BaF}_2$  and 2 moles  $\text{H}_2\text{SO}_4$  is to be made neutral by adding  $\text{Ca}(\text{OH})_2$ . Moles of  $\text{Ca}(\text{OH})_2$  required .....
3. If  $[\text{BaCl}_2] = 0.05 \text{ M}$  then  $p_{\text{Cl}^-} = \dots\dots\dots$
4. 2.78 g  $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$  in 100 mL solution gives 0.1 M solution. Thus,  $x = \dots\dots\dots$
5. 25 mL of a solution containing  $6.1 \text{ g L}^{-1}$  of an oxalate of formula  $\text{K}_x\text{H}_y(\text{C}_2\text{O}_4)_z \cdot n\text{H}_2\text{O}$  required 18 mL of 0.1 N NaOH and 24 mL of 0.1 N  $\text{KMnO}_4$  in two separate titrations.  
Thus,  $x = \dots\dots\dots$
6. Thus,  $y = \dots\dots\dots$
7. Thus,  $z = \dots\dots\dots$
8. Thus,  $n = \dots\dots\dots$

(Refer Problem 15 (P-323) for solution of Question 5-8)

# Answers & Solutions

## Master Exercises

### Exercise 1

#### Short Answer Type Questions

1.  $\text{NaOH} = 0.125 \text{ M}$

Volume =  $V$  (in litres) = ?

Amount = 4.0 g

$$MV = \text{moles} = \text{moles} \times 40 \text{ g}$$

$$0.125 \times V = \text{moles}$$

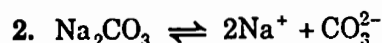
$$0.125 \times V \times 40 = 4 \text{ g (given)}$$

$$V = 0.8 \text{ L} = 800 \text{ mL}$$

or  $w = \frac{MmV}{1000}$

$$\text{Amount in grams} = \frac{\text{molarity} \times \text{molar mass} \times \text{volume (in mL)}}{1000}$$

$$\therefore \bar{V} = \frac{1000w}{Mm} = \frac{1000 \times 4}{0.125 \times 40} = 800 \text{ mL}$$



$$\text{Moles of Na}_2\text{CO}_3 = \frac{1.06}{106} = 0.01 \text{ mol}$$

$$\text{Volume} = 250 \text{ mL} = 0.250 \text{ L}$$

$$\text{Molarity} = \frac{\text{mole}}{\text{litre}} = \frac{0.010}{0.250} = 0.04 \text{ M}$$

$$\therefore [\text{Na}^+] = 0.08 \text{ M}$$

$$[\text{CO}_3^{2-}] = 0.04 \text{ M}$$

3. (a)  $[\text{NH}_4^+] = 0.50 \text{ M}$ ,  $[\text{SO}_4^{2-}] = 0.25 \text{ M}$

(b)  $[\text{Na}^+] = 0.246 \text{ M}$ ,  $[\text{CO}_3^{2-}] = 0.123 \text{ M}$

(c)  $[\text{H}^+] = [\text{NO}_3^-] = 0.056 \text{ M}$

4. For dilution

$$M_1V_1 = M_2V_2$$

before after

$$1.50 \times 25.0 = M_2 \times 500$$

$$M_2 = \frac{1.50 \times 25.0}{500}$$

$$= 0.75 \text{ M}$$

5.

$$M_1V_1 = M_2V_2$$

$$6.00 \times 20.8 = M_2 \times 1000$$

$$M_2 = 0.125 \text{ M of volume 1 L}$$

(b) 50.0 mL of 3.00 M is diluted to 1000 mL

$$M_1V_1 = M_2V_2$$

$$3.00 \times 50.0 = M_2 \times 1000$$

$$M_2 = 0.15 \text{ M}$$

Thus, method (a) is employed.

6. Moles of  $\text{NaCl} = 1.00 \times 0.225$

$$= 0.225 \text{ mol}$$

$$\text{Moles of PbCl}_2 = V (\text{required}) \times 0.750$$

$$2 \text{ mol NaCl react with} = 1 \text{ mol of Pb(NO}_3)_2$$

$$\text{Thus, } 0.225 \text{ mol reacts with} = 0.1125 \text{ mol Pb(NO}_3)_2$$

$$\therefore V \times 0.750 = 0.1125$$

$$V = 0.15 \text{ L}$$

$$= 150 \text{ mL}$$

7. Method I: In terms of moles

$$\text{Volume of HCl} = 38.55 \text{ mL}$$

$$= 0.03855 \text{ L}$$

$$\text{Moles of HCl} = 0.03855 \times \text{molarity (required)}$$

$$\text{Moles of Na}_2\text{CO}_3 = \frac{2.150}{106} = 0.0203$$

Based on reaction

$$1 \text{ mol Na}_2\text{CO}_3 \text{ reacts with} = 2 \text{ mol HCl}$$

$$\therefore 0.0203 \text{ mol Na}_2\text{CO}_3 \text{ reacts with} = 0.0406 \text{ mol HCl}$$

$$\therefore 0.03855 \times M = 0.0406$$

$$M = 1.05 \text{ M}$$

Method II: In terms of equivalent

In any reaction.

$$\text{Equivalent of reactant I} = \text{Equivalent of reactant II}$$

$$\text{Equivalent of Na}_2\text{CO}_3 = \frac{2.150}{53 (\text{equivalent mass})}$$

$$\text{Equivalent of HCl} = \frac{NV}{1000} = \frac{N \times 38.55}{1000}$$

$$\therefore \frac{N \times 38.55}{1000} = \frac{2.150}{53}$$

$$N(\text{HCl}) = 1.05 \text{ N}$$

$$\therefore M(\text{HCl}) = N(\text{HCl}) = 1.05 \text{ N}$$

8. As above

$$\text{Equivalent of H}_2\text{A} = \text{Equivalent of KOH}$$

$$\text{Equivalent of H}_2\text{A} = \frac{0.490}{E}$$

$$\text{Equivalent of KOH} = \frac{100 \times 0.1}{1000}$$

$$= 0.01$$

$$\therefore \frac{0.49}{E} = 0.01$$

$$\therefore E = 49 \text{ g equivalent}^{-1}$$

$\text{H}_2\text{A}$  is a dibasic acid, hence,

$$\begin{aligned}\text{molar mass of H}_2\text{A} &= 2 \times \text{equivalent mass} \\ &= 98 \text{ g mol}^{-1}\end{aligned}$$

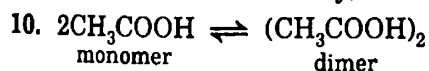
9. (a) Glucose is non-electrolyte



(c) AgI is insoluble in  $\text{H}_2\text{O}$

(d) LiCl behaves like non-electrolyte in ether.

Hence, in (a), (c) and (d), analytical and equilibrium concentrations (molarity) are identical.

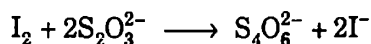
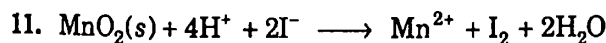


In benzene, there is 100% dimer formation of acetic acid. Thus, molecular weight of acetic acid in benzene =  $120 \text{ g mol}^{-1}$

$$\begin{aligned}\therefore [\text{CH}_3\text{COOH}]_{\text{eq}} &= 0.0 \text{ M} \\ [(\text{CH}_3\text{COOH})_2]_{\text{eq}} &= 0.5 \text{ M}\end{aligned}$$

Note: If  $\text{CH}_3\text{COOH}$  (without dimer) =  $1 \text{ M}$  it means  $60 \text{ g L}^{-1}$  of solution. But when dimer is formed

$$\begin{aligned}\text{equilibrium molarity} &= \frac{60 \text{ g L}^{-1}}{120 \text{ g mol}^{-1}} \\ &= 0.5 \text{ mol L}^{-1}\end{aligned}$$



**Method I:** (Based on number of equivalents)

Equivalent of  $\text{MnO}_2 \equiv$  equivalents of  $\text{S}_2\text{O}_3^{2-}$

Equivalent mass of  $\text{MnO}_2 = 43.5$

$$0.07220 \text{ M S}_2\text{O}_3^{2-} \equiv 0.07220 \text{ N S}_2\text{O}_3^{2-}$$

$$\text{Equivalents of S}_2\text{O}_3^{2-} = \frac{0.07220 \times 32.30}{1000} = 2.332 \times 10^{-3}$$

$$\text{Equivalents of MnO}_2 = 2.332 \times 10^{-3}$$

$$\begin{aligned}\therefore \text{Pure MnO}_2 \text{ in the sample} &= 2.332 \times 10^{-3} \times 43.5 \text{ g} \\ &= 0.1014 \text{ g} \\ \% \text{ of pure MnO}_2 &= \frac{0.1014}{0.1344} \times 100 \\ &= 75.48\%\end{aligned}$$

**Method II:** (Based on stoichiometric coefficients)

$$\text{Numbr of moles S}_2\text{O}_3^{2-} = \frac{32.30 \times 0.0722}{1000}$$

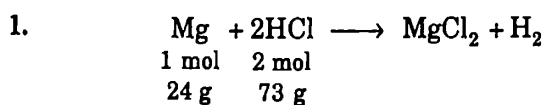
$$= 2.332 \times 10^{-3} \text{ mol}$$

$$\text{Number of moles of MnO}_2 = \frac{\text{mol of S}_2\text{O}_3^{2-}}{2}$$

$$= 1.166 \times 10^{-3} \text{ mol}$$

$$\begin{aligned}\text{Pure MnO}_2 \text{ in the sample} &= 1.166 \times 10^{-3} \times 87 \text{ g} \\ \% \text{ MnO}_2 &= 75.48\%\end{aligned}$$

## Analytical Questions

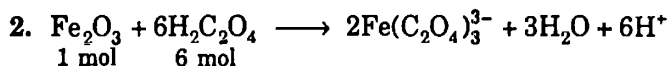


$$\begin{aligned}\text{HCl} &= 5 \times 10^2 \times 2 \text{ millimol} \\ &= 1000 \text{ millimol} = 1 \text{ mol}\end{aligned}$$

$$\text{Mg} = 4.47 \text{ g} = 0.18625 \text{ mol}$$

$$\text{HCl required} = 0.3725 \text{ mol}$$

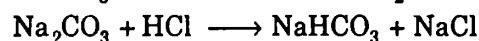
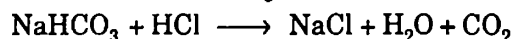
$$\begin{aligned}\therefore \text{HCl unreacted} &= (1 - 0.3725) \text{ mol in } 500 \text{ mL solution} \\ \text{Molarity of HCl} &= \frac{0.6275}{0.5} = 1.255 \text{ M}\end{aligned}$$



$$\text{Oxalic acid taken} = 500 \times 1 = 500 \text{ millimol} = 0.5 \text{ mol}$$

$$\begin{aligned}\therefore \text{Fe}_2\text{O}_3 \text{ required} &= \frac{0.5}{6} \text{ mol} = \frac{1}{12} \text{ mol} \\ &= \frac{1}{12} \times 160 = 13.33 \text{ g}\end{aligned}$$

3.  $\text{NaHCO}_3$  is completely neutralised and  $\text{Na}_2\text{CO}_3$  is neutralised to phenolphthalein end point indicating neutralisation upto  $\text{NaHCO}_3$



$$\text{Thus, } 0.2 \text{ M NaHCO}_3 = 0.2 \text{ N NaHCO}_3$$

$$\text{and } 0.2 \text{ M Na}_2\text{CO}_3 = 0.2 \text{ N Na}_2\text{CO}_3$$

$$\underbrace{N_1 V_1}_{\text{acid}} = \underbrace{N_2 V_2}_{\text{base (Na}_2\text{CO}_3 \text{ and NaHCO}_3)}$$

$$30x = 10 \times 0.2 + 5 \times 0.2$$

$$x = 0.1 \text{ M}$$

4. Solution is acidic ( $\text{pH} = 1$ )

$$[\text{H}^+] = 10^{-\text{pH}} \text{ M}$$

$$\therefore [\text{H}^+] = 10^{-1} \text{ M}$$

Let molarity of  $\text{H}_2\text{SO}_4$  or  $\text{Ba}(\text{OH})_2 = 1 \text{ M}$

$$\therefore \text{Normality} = 2 \text{ M}$$

$$\therefore N_1 V_1 (\text{acid}) = 300 \times 2 = 600 \text{ M}$$

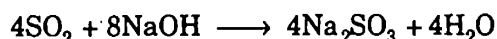
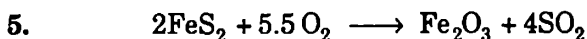
$$N_2 V_2 (\text{base}) = 200 \times 2 = 400 \text{ M}$$

$$N(\text{H}^+) = \frac{N_1 V_1 - N_2 V_2}{V_1 + V_2}$$

$$0.1 = \frac{200 \text{ M}}{500}$$

$$M = \frac{0.1 \times 500}{200} = 0.25$$

$$\therefore \text{Normality} = 2 \text{ M} = 0.5 \text{ N}$$



$$\text{Thus, } 2\text{FeS}_2 \equiv 4\text{SO}_2 \equiv 8\text{NaOH}$$

$$\therefore 1 \text{ FeS}_2 \equiv 4 \text{ NaOH}$$

$$\begin{aligned}\text{FeS}_2 \text{ in } 1000 \text{ kg } (10^6 \text{ g coal}) &= 10^6 \times \frac{0.05}{100} = 500 \text{ g} \\ &= \frac{500}{120} = 4.167 \text{ mol}\end{aligned}$$

$$\therefore \text{NaOH required} = 16.67 \text{ mol}$$

$$6 \text{ M NaOH contains } 6 \text{ mol NaOH in } = 1000 \text{ mL}$$

$$\begin{aligned}\therefore 16.67 \text{ mol are in} &= \frac{1000 \times 16.67}{6} \text{ mL} \\ &= 2778 \text{ mL}\end{aligned}$$

$$\text{or } \frac{MV}{1000} = \text{mol}$$

$$\frac{6 \times V}{1000} = 16.67$$

$$\therefore V = 2778 \text{ mL}$$

6. Phenolphthalein indicates 50% reaction of  $\text{Na}_2\text{CO}_3$  (upto  $\text{NaHCO}_3$ ) and 100% reaction of  $\text{NaOH}$  while methyl orange indicates 100% reaction of both.

Let volume of 0.995 N  $\text{HCl}$  required by  $\text{Na}_2\text{CO}_3 = x \text{ mL}$   
and by  $\text{NaOH} = y \text{ mL}$

with phenolphthalein

$$\frac{x}{2} + y = 19.5 \text{ mL}$$

with methyl-orange

$$x + y = 25.9 \text{ mL}$$

$$\therefore x = 12.8 \text{ mL}$$

$$\therefore y = 13.1 \text{ mL}$$

$$N_1 V_1 = N_2 V_2$$

$$\text{Na}_2\text{CO}_3 \quad \text{HCl}$$

$$N_1 \times 25 = 0.995 \times 12.8$$

$$N_1(\text{Na}_2\text{CO}_3) = 0.50944 \text{ N}$$

$$= 0.50944 \times 53$$

$$= 27.0 \text{ gL}^{-1}$$

$$N_1 V_1 = N_2 V_2$$

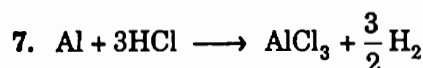
$$\text{NaOH} \quad \text{HCl}$$

$$N_1 \times 25 = 0.995 \times 13.1$$

$$N_1(\text{NaOH}) = 0.5214 \text{ N}$$

$$= 0.5214 \times 40$$

$$= 20.86 \text{ gL}^{-1}$$



$$\therefore \frac{0.05 \times 12}{1000} \text{ mol HCl} = \frac{0.05 \times 12}{1000 \times 3} \text{ mol Al}$$

$$= 2 \times 10^{-4} \text{ mol Al}$$

$$= 2 \times 10^{-4} \times 27 \text{ g Al}$$

$$= \frac{2 \times 10^{-4} \times 27}{2.7} \text{ cm}^3 \text{ Al}$$

$$= 2 \times 10^{-3} \text{ cm}^3 \text{ Al}$$

$$\left( \text{volume} = \frac{\text{mass}}{\text{density}} \right)$$

$$\text{thickness} \times \text{area} = \text{volume}$$

$$\frac{0.1}{10} \times \text{area} = 2 \times 10^{-3}$$

$$\therefore \text{area} = 0.2 \text{ cm}^2$$

8.  $\text{Na}_2\text{B}_4\text{O}_7$  borax behaves like a weak base

0.7439 g sample of borax  $\equiv$  31.64 mL of 0.108 M  $\text{HCl}$

Based on reaction

$$\frac{\text{moles of } \text{Na}_2\text{B}_4\text{O}_7}{\text{moles of HCl}} = \frac{1}{2}$$

$$\text{Moles of HCl} = \frac{31.64 \times 0.108}{1000}$$

$$= 3.417 \times 10^{-3} \text{ mol}$$

$$\therefore \text{Moles of } \text{Na}_2\text{B}_4\text{O}_7 = 1.7085 \times 10^{-3} \text{ mol}$$

$$\therefore \text{Na}_2\text{B}_4\text{O}_7 = 1.7085 \times 10^{-3} \times 202 \text{ g}$$

$$= 0.3451 \text{ g in } 0.7439 \text{ g borax}$$

$$(a) \text{ Per cent } \text{Na}_2\text{B}_4\text{O}_7 = 46.39\%$$

$$(b) \text{ Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} = 1.7085 \times 10^{-3} \times 382 \text{ g}$$

$$\text{Per cent } \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} = 87.73\%$$

$$(c) \text{ B}_2\text{O}_3 = 2 \times \text{moles of } \text{Na}_2\text{B}_4\text{O}_7$$

$$= 2 \times 1.7085 \times 10^{-3} \times 70 \text{ g}$$

$$= 0.2392 \text{ g}$$

$$\text{Per cent } \text{B}_2\text{O}_3 = 32.15\%$$

$$(d) \text{ Na}_2\text{B}_4\text{O}_7 = 4 \text{ B} = 4 \times 1.7085 \times 10^{-3} \text{ mol}$$

$$= 4 \times 1.7085 \times 10^{-3} \times 11 \text{ g}$$

$$\therefore \text{B} = 0.0752 \text{ g}$$

$$\text{Per cent} = 10.11\%$$

9. (a) 100 mL of serum has  $\text{K}^+ = 18 \text{ mg}$

$$= 18 \times 10^{-3} \text{ g}$$

$$= \frac{18 \times 10^{-3}}{39} \text{ mol}$$

$$\therefore [\text{K}^+] = \frac{18 \times 10^{-3}}{39} / 0.1$$

$$= 4.615 \times 10^{-3} \text{ M}$$

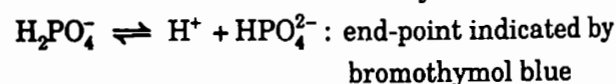
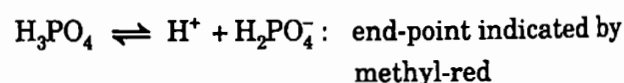
$$\text{Similarly, } [\text{Cl}^-] = \frac{365 \times 10^{-3}}{35.5} / 0.1$$

$$= 0.103 \text{ M}$$

$$(b) p_{\text{K}^+} = -\log [\text{K}^+] = 2.336$$

$$p_{\text{Cl}^-} = -\log [\text{Cl}^-] = 0.988$$

10.  $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$  : end-point indicated by methyl-red



Let  $\text{HCl} = x \text{ millimol}$

$\text{H}_3\text{PO}_4 = y \text{ millimol}$

then  $x + y$  (first ionisation step)  $= 35 \times 0.1 = 3.5 \text{ millimol}$

$y$  (second ionisation step)  $= 15 \times 0.1 = 1.5 \text{ millimol}$

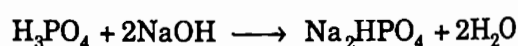
$$\therefore \text{HCl} = 3.5 - 1.5 = 2.00 \text{ millimol}$$

and  $\text{H}_3\text{PO}_4 = 1.5 \text{ millimol}$

$$11. \text{ Let } \text{P}_2\text{O}_5 = x \text{ g} = \frac{x}{142} \text{ mol} = \frac{2x}{142} \text{ mol } \text{H}_3\text{PO}_4$$

(since one mole of  $\text{P}_2\text{O}_5$  in aqueous solution forms 2 moles  $\text{H}_3\text{PO}_4$ )

$$\therefore \text{H}_3\text{PO}_4 = (0.405 - x) \text{ g} = \left( \frac{0.405 - x}{98} \right) \text{ mol}$$



$$\text{NaOH required by } \text{P}_2\text{O}_5 = \frac{4x}{142} \text{ mol} = \frac{2x}{71}$$

**= 0.2314 mg per mL blood**



18. Let molar mass of the reductant =  $m \text{ g mol}^{-1}$

$$\therefore \text{Molarity} = \frac{2.52}{m} \text{ mol L}^{-1}$$

$$0.01 \text{ M MnO}_4^- = 0.05 \text{ N MnO}_4^-$$

$$25 \text{ mL of } N_1 \text{ (reductant)} = 20 \times 0.05 \text{ N MnO}_4^-$$

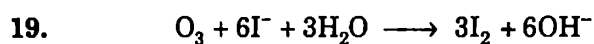
$$\therefore N_1 \text{ (reductant)} = \frac{20 \times 0.05}{25} = 0.04 \text{ N}$$

Change in oxidation state of reductant = 2 units

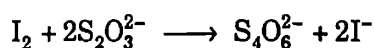
$$\therefore \text{Molarity (reductant)} = 0.02 \text{ M}$$

$$\therefore 0.02 = \frac{2.52}{m}$$

$$\therefore m = 126 \text{ g mol}^{-1}$$



$$\text{Eq. wt. of O}_3 = \frac{M}{6} = \frac{48}{6} = 8$$



Equivalent of  $\text{S}_2\text{O}_3^{2-}$  = Equivalent of  $\text{I}_2$  = Equivalent of

$$\text{O}_3 = \frac{1.5 \times 0.01}{1000} = 1.5 \times 10^{-5}$$

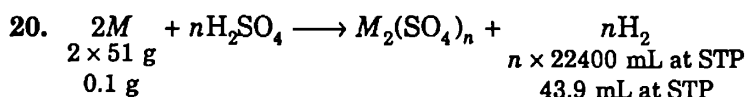
$$\therefore = \frac{1.5 \times 10^{-5}}{6} \text{ mol}$$

$$\text{Air taken} = \frac{pV}{RT} = \frac{1 \times 10}{0.0821 \times 300} \text{ mol}$$

$$= 0.406 \text{ mol}$$

$$\therefore \text{Mol \% of O}_3 \text{ in air} = \frac{1.5 \times 10^{-5} \times 100}{6 \times 0.406}$$

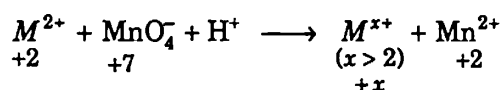
$$= 6.16 \times 10^{-4} \%$$



$$\frac{2 \times 51}{0.1} = \frac{n \times 22400}{43.9}$$

$$\therefore n = 2$$

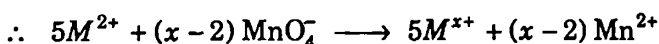
$M$  is oxidised to  $M^{2+}$  by  $\text{H}_2\text{SO}_4$



$$\text{Also } 0.1 \text{ N MnO}_4^- = 0.02 \text{ M MnO}_4^-$$

$$\therefore \text{Change in oxidation number of } M^{2+} = (x - 2)$$

$$\text{Change in oxidation number of MnO}_4^- = 5$$



$$\therefore \frac{\text{moles of } M^{2+}}{\text{moles of MnO}_4^-} = \frac{5}{x - 2} = \frac{0.1/51}{58.8 \times 0.02/1000}$$

$$\therefore x = 3$$

$$\begin{aligned} [58.8 \text{ mL of } 0.1 \text{ N MnO}_4^- &= 58.8 \text{ mL of } 0.02 \text{ M MnO}_4^- \\ &= \frac{58.8 \times 0.02}{1000} \text{ mol}] \end{aligned}$$

21. Let  $\text{XO} = w \text{ g} = \frac{w}{(X + 16)} \text{ mol}$

and  $\text{X}_2\text{O}_3 = (2.18 - w) \text{ g} = \frac{2.18 - w}{(2X + 48)} \text{ mol}$

$$\text{Number of moles of Cr}_2\text{O}_7^{2-} \text{ required by XO} = \frac{5w}{6(X + 16)}$$

$$\begin{aligned} \text{Number of moles of Cr}_2\text{O}_7^{2-} \text{ required by X}_2\text{O}_3 \\ = \frac{4(2.18 - w)}{3(2X + 48)} \end{aligned}$$

$$\text{Number of moles of XO}_4^- \text{ from XO} = \frac{w}{(X + 16)}$$

$$\text{Number of moles of XO}_4^- \text{ from X}_2\text{O}_3 = \frac{2(2.18 - w)}{(2X + 48)}$$

$$\therefore \frac{5w}{6(X + 16)} + \frac{4(2.18 - w)}{3(2X + 48)} = 0.015$$

and  $\frac{w}{(X + 16)} + \frac{2(2.18 - w)}{(2X + 48)} = 0.0187$

$$\frac{2.18 - w}{2X + 48} = 0.0018$$

On solving  $w = 1.7372 \text{ g}$  and  $X = 99$

22.  $24 \text{ g K}_2\text{CrO}_4 = \frac{24}{194} \text{ mol} = 0.1237 \text{ mol}$

$$\text{N}_2\text{H}_4 \text{ used} = 0.1237 \times \frac{3}{4}$$

$$= 0.0928 \text{ mol}$$

$$= 0.0928 \times 32 \text{ g}$$

$$= 2.969 \text{ g}$$

23. Moles of  $\text{K}_2\text{Cr}_2\text{O}_7 = \frac{4.23 \times 0.07654}{1000} = 3.24 \times 10^{-4} \text{ mol}$

$$\therefore \text{CH}_3\text{CH}_2\text{OH oxidised} = 3.24 \times 10^{-4} \times \frac{3}{2} \text{ mol}$$

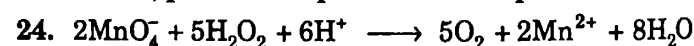
$$= 4.86 \times 10^{-4} \text{ mol}$$

$$= 4.86 \times 10^{-4} \times 46 \text{ g}$$

$$= 0.0223 \text{ g in } 10 \text{ g sample of blood}$$

$$= 0.223\% \text{ above } 0.1\% \text{ prescribed limit}$$

Hence, police will prosecute the person.

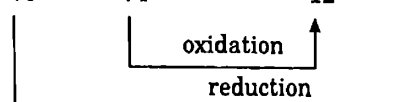
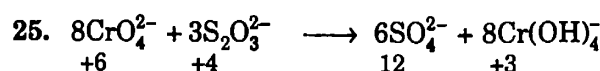


$$\text{Pure H}_2\text{O}_2 = \frac{x}{100} \text{ g} = \frac{x}{1700} \text{ equivalent}$$

$$\text{MnO}_4^- \text{ used} = \frac{Nx}{1000} \text{ equivalent}$$

$$\therefore \frac{Nx}{1000} = \frac{x}{1700}$$

$$N(\text{MnO}_4^-) = \frac{10}{17}$$



$$0.154 \text{ M CrO}_4^{2-} = 0.154 \times 3 \text{ N CrO}_4^{2-}$$

$$0.246 \text{ M S}_2\text{O}_3^{2-} = 0.246 \times 8 \text{ N S}_2\text{O}_3^{2-}$$

$$\therefore N_1 V_1 = N_2 V_2$$

$$V \times 0.154 \times 3 = 0.246 \times 8 \times 40$$

$$V = 170.4 \text{ mL}$$

Note : Oxidation number of two S-atoms in  $\text{S}_2\text{O}_3^{2-} = 4$  and that of in  $\text{SO}_4^{2-} = 12$

26.  $\text{K}_2\text{Cr}_2\text{O}_7$  is required by oxidation of  $\text{FeSO}_4$  only

$\text{Fe}_2(\text{SO}_4)_3$  is already in oxidised state. However, metallic zinc reduces  $\text{Fe}_2(\text{SO}_4)_3$  to  $\text{FeSO}_4$  and thus,

$$N(\text{FeSO}_4 \text{ before reduction}) = \frac{22.45 \times 0.1}{25}$$

$$= 0.0898 \text{ N}$$

$$N(\text{FeSO}_4 \text{ after reduction}) = \frac{34.25 \times 0.1}{25}$$

$$= 0.137 \text{ N}$$

$$\therefore N[\text{total FeSO}_4 \text{ and Fe}_2(\text{SO}_4)_3] = 0.137 \text{ N}$$

$$\therefore \text{FeSO}_4 \text{ in mixture} = 0.0898 \times 152$$

$$= 13.6496 \text{ gL}^{-1}$$

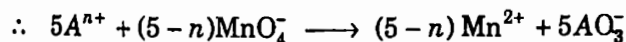
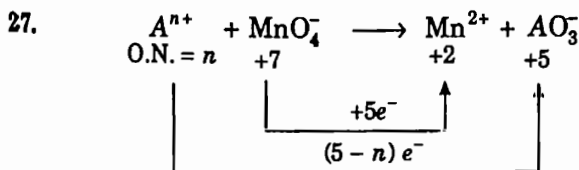
$$N(\text{Fe}_2(\text{SO}_4)_3) = 0.137 - 0.0898$$

$$= 0.0472 \text{ N}$$

$$\therefore \text{Fe}_2(\text{SO}_4)_3 \text{ in mixture} = 9.44 \text{ gL}^{-1}$$

$$(\text{Eq. wt. of FeSO}_4 = 152 \text{ g equiv}^{-1},$$

$$\text{Fe}_2(\text{SO}_4)_3 = 200 \text{ g equiv}^{-1})$$



$$\therefore \frac{5 \text{ mol of A}^{n+}}{(5-n) \text{ mol of MnO}_4^-} = \frac{2.68 \times 10^{-3}}{1.61 \times 10^{-3}}$$

$$5 - n = 3$$

$$\therefore n = 2$$

$\therefore$  Chloride is  $\text{AlCl}_3$

$$\therefore \text{Equivalent wt. of AlCl}_3 = \frac{\text{molar mass}}{\text{change in O.N.}}$$

$$= \frac{97 + 71}{3} = 56$$

28.  $40 \text{ mL of } 0.05 \text{ M MnO}_4^- = 40 \text{ mL of } 0.05 \times 5 \text{ N MnO}_4^-$

$$= 10 \text{ milliequivalent}$$

$$= 0.01 \text{ equivalent}$$

$$\therefore \text{C}_2\text{O}_4^{2-} = 0.01 \text{ equivalent}$$

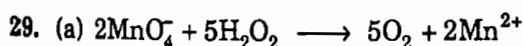
$$\text{CaO} = 0.01 \text{ equivalent}$$

$$= 0.005 \text{ mol}$$

$$= 0.005 \times 56 \text{ g} = 0.28 \text{ g}$$

$$\text{in } 0.518 \text{ g sample of limestone}$$

$$\therefore \% \text{ of CaO} = 54.05\%$$



$$\text{Moles of KMnO}_4 = \frac{0.316}{158} = 2 \times 10^{-3} \text{ mol}$$

$$\therefore \text{H}_2\text{O}_2 = \frac{5}{2} \times 2 \times 10^{-3} \text{ mol pure}$$

$$= 5 \times 10^{-3} \text{ mol pure}$$

$$= 0.17 \text{ g pure H}_2\text{O}_2 \text{ in } 0.2 \text{ g sample}$$

$$\therefore \% \text{ of pure H}_2\text{O}_2 = 85\%$$



$\text{O}_2$  formed from  $0.17 \text{ g pure H}_2\text{O}_2$

$$= \frac{32}{34} \times 0.17 \text{ g} = 0.16 \text{ g}$$

$$= \frac{0.16}{32} \text{ mol}$$

$$= 5.0 \times 10^{-3} \text{ mol}$$

$$pV = nRT$$

$$\therefore V = \frac{nRT}{p} = \frac{5.0 \times 10^{-3} \times 0.0821 \times 300}{(750/760)}$$

$$= 0.1248 \text{ L} = 124.8 \text{ mL}$$

30. Let  $\text{Na}_2\text{C}_2\text{O}_4 = x \text{ g} = \frac{x}{134} \text{ mol} = \frac{x}{134} \text{ mol C}_2\text{O}_4^{2-}$

$$\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 = y \text{ g} = \frac{y}{218} \text{ mol} = \frac{2y}{218} \text{ mol C}_2\text{O}_4^{2-}$$

and  $\frac{3y}{218} \text{ mol H}^+$

$$\text{Total C}_2\text{O}_4^{2-} = \left( \frac{x}{134} + \frac{2y}{218} \right) \text{ mol}$$

$$\text{Total H}^+ = \frac{3y}{218} \text{ mol}$$

If volume of the solution is  $V$  litres, then

$$M(\text{C}_2\text{O}_4^{2-}) = \left( \frac{x}{134} + \frac{2y}{218} \right) / V$$

$$\therefore N(\text{C}_2\text{O}_4^{2-}) = 2 \left( \frac{x}{134} + \frac{2y}{218} \right) / V$$

$$N(\text{H}^+) = \frac{3y}{218} / V$$

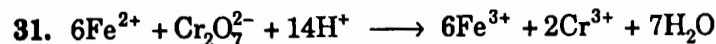
$\text{C}_2\text{O}_4^{2-}$  is a reducing agent and  $\text{H}^+$  is an acid.

Given,  $N(\text{C}_2\text{O}_4^{2-}) = 3.62 \text{ N}(\text{H}^+)$

$$\therefore \frac{2 \left( \frac{x}{134} + \frac{2y}{218} \right)}{V} = \frac{3.62 \times 3y}{218} / V$$

$$\frac{x}{134} + \frac{2y}{218} = \frac{3.62 \times 1.5y}{218}$$

$$\frac{x}{y} = 2.1 : 1$$



$$1000 \text{ mL contains} = 5.442 \text{ g K}_2\text{Cr}_2\text{O}_7 = \frac{5.442}{294} \text{ mol}$$

$$= 0.01851 \text{ mol K}_2\text{Cr}_2\text{O}_7$$

$$= 0.01851 \times 6 \text{ mol Fe}^{2+}$$

$$= \frac{0.01851 \times 6}{3} \text{ mol Fe}_3\text{O}_4$$

$$= 0.03702 \text{ mol Fe}_3\text{O}_4$$

$$= 0.03702 \times 232 \text{ g Fe}_3\text{O}_4$$

$$\therefore \text{Fe}_3\text{O}_4 \text{ per mL} = 8.59 \times 10^{-3} \text{ g}$$

32.  $\text{MnO}_2 + 4\text{HCl} \longrightarrow \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$   
 $\text{Cl}_2 + 2\text{KI} \longrightarrow 2\text{KCl} + \text{I}_2$   
 $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$   
 $2\text{Na}_2\text{S}_2\text{O}_3 \equiv \text{I}_2 \equiv \text{Cl}_2 \equiv \text{MnO}_2$   
Moles of  $\text{Na}_2\text{S}_2\text{O}_3$  used =  $\frac{30 \times 0.1}{1000} = 3 \times 10^{-4}$  mol  
 $\therefore$  Moles of pure  $\text{MnO}_2 = \frac{30 \times 10^{-4}}{2}$  mol  
 $= \frac{30 \times 10^{-4}}{2} \times 87 \text{ g pure MnO}_2$   
 $= 0.1305 \text{ g in } 0.5 \text{ g impure MnO}_2$   
 $\therefore$  % purity =  $\frac{0.1305}{0.5} \times 100 = 26.1\%$
33.  $10 \text{ mL of } N_1 \text{ MnO}_4^- = 50 \text{ mL of } 1.0 \text{ N I}^-$   
 $\therefore 10 \times N_1 = 50 \times 1$   
 $\therefore N_1 = 5 \text{ N}$   
Equivalent of  $\text{KMnO}_4 = \frac{5 \times 100}{1000} = 0.5$   
 $\therefore$  Equivalents of oxalic acid = 0.5  
 $\therefore$  Mass of oxalic acid =  $0.5 \times 45 \text{ g} = 22.5 \text{ g}$

34.  $\text{CaOCl}_2 + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + \text{Cl}_2$   
 $\text{Cl}_2 + 2\text{KI} \longrightarrow 2\text{KCl} + \text{I}_2$   
 $\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$   
 $\text{CaOCl}_2 \equiv \text{Cl}_2 \equiv \text{I}_2 \equiv 2\text{Na}_2\text{S}_2\text{O}_3$   
 $\therefore$  Equivalent mass of  $\text{Cl}_2 = \frac{71}{2} = 35.5$
- $\therefore$   $\frac{N_1 V_1}{\text{Cl}_2 \text{ in bleaching powder}} = \frac{N_2 V_2}{\text{hypo}}$   
 $N_1 \times 20 = 0.1 \times 20$   
 $\therefore N_1 = 0.1 \text{ N}$   
 $\therefore \text{CaOCl}_2 = 0.1 \text{ N}$   
 $\therefore \text{Cl}_2 = 0.1 \times 35.5 \text{ g L}^{-1}$   
 $= 3.55 \text{ g L}^{-1} \text{ (pure)}$   
Impure sample =  $\frac{5.0 \text{ g}}{0.5 \text{ L}} = 10 \text{ g L}^{-1}$   
 $\therefore$  % of pure  $\text{Cl}_2 = \frac{3.55}{10} \times 100$   
 $= 35.5\%$

## Exercise 2

### Only One Option Correct

1.  $100 \text{ mL of } 0.40 \text{ M KCl} = 0.04 \text{ mol KCl}$   
 $100 \text{ mL of } 0.50 \text{ M KCl} = 0.05 \text{ mol KCl}$   
Thus,  $\text{KCl required} = 0.05 - 0.04$   
 $= 0.01 \text{ mol}$   
 $= 0.01 \times 74.5 \text{ g}$   
 $= 0.745 \text{ g KCl}$

Hence, (a)

2.  $\text{H}_3\text{PO}_4 = 10.75 \text{ g in } 550 \text{ mL}$   
 $= \frac{10.75}{98} \text{ mol in } 0.550 \text{ L}$   
 $[\text{H}_3\text{PO}_4] = \frac{10.75/98}{0.550} \text{ mol L}^{-1} = 0.20 \text{ M}$

But it is 0.40 N

Hence, change in oxidation number = 2 units

or  $\text{H}^+$  neutralised = 2

In (a)  $\text{H}_3\text{PO}_4$  changes to  $\text{HPO}_4^{2-}$

Hence, (a)

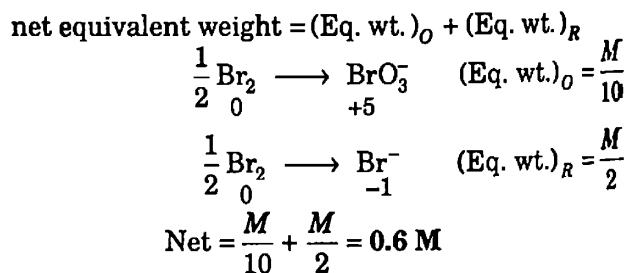
3.  $\text{H}_2\text{S} \longrightarrow \text{SO}_2$   
 $\uparrow \quad \quad \uparrow$   
 $-2 \quad \quad +4$

Change in oxidation number = 6 unit

$\therefore 1 \text{ mol H}_2\text{S} = 6 \text{ equivalents H}_2\text{S}$

Hence, (c)

4. In the disproportionation reaction



Hence, (c)

5. (c)  
6.  $20.00 \text{ mL of } 0.1 \text{ M Pb}^{2+} = 2 \times 10^{-3} \text{ mol Pb}^{2+}$   
 $30.00 \text{ mL of } 0.1 \text{ M SO}_4^{2-} = 3 \times 10^{-3} \text{ mol SO}_4^{2-}$   
 $\text{Pb}^{2+} + \text{SO}_4^{2-} \longrightarrow \text{PbSO}_4$   
 $\text{Pb}^{2+}$  is in the limiting a quantity and every 1 mol of  $\text{Pb}^{2+}$  gives equal mole of  $\text{PbSO}_4$  hence,  $\text{PbSO}_4$  formed = 0.002 mol.

Hence, (a)

7.  $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$   
 $\text{Na}_2\text{SO}_4 \rightleftharpoons 2\text{Na}^+ + \text{SO}_4^{2-}$   
 $[\text{Na}^+]_{\text{mix}} = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$   
 $= \frac{0.12 \times 30 + 0.30 \times 70}{30 + 70}$   
 $= 0.246$

Hence, (d)

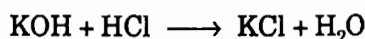
$$8. \quad M_1 V_1 (\text{HCl, acid}) = 16$$

$$M_2 V_2 (\text{KOH, base}) = 18 > M_1 V_1 (\text{acid})$$

Mixture is basic.

$$[\text{KOH}]_{\text{mix}} = \frac{M_2 V_2 - M_1 V_1}{V_1 + V_2}$$

$$= \frac{18 - 16}{200} = 0.01 \text{ M}$$



KCl is from HCl and 80 mL of 0.2 M HCl is diluted to 200 mL

$$80 \times 0.2 = M(\text{KCl}) \times 200$$

$$M(\text{KCl}) = 0.08 \text{ M}$$

Thus, resultant mixture has KOH (0.01 M) and KCl (0.08 M)

Hence, (c)

9.  $\text{K}^+$  and  $\text{Cl}^-$  remain unchanged but due to dilution (in equal volumes), molar concentration of each is halved.

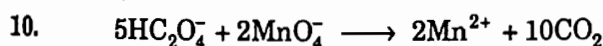
$$[\text{Cl}^-] = 0.1 \text{ M}$$

$$[\text{K}^+] = 0.2 \text{ M}$$

Also,  $[\text{OH}^-] > [\text{H}^+]$ , mixture is basic

$$[\text{OH}^-]_{\text{mix}} = \frac{0.4 - 0.2}{2} = 0.1 \text{ M}$$

Hence, (c)



$$100 \text{ mL of } 0.02 \text{ M MnO}_4^- = 0.002 \text{ mol MnO}_4^-$$

$$= 0.005 \text{ mol of HC}_2\text{O}_4^- = x$$

$$100 \text{ mL of } 0.05 \text{ M Ca(OH)}_2$$

$$= \frac{100 \times 0.05}{1000} \text{ mol Ca(OH)}_2$$

$$= 0.005 \text{ mol Ca(OH)}_2$$

$$= 0.01 \text{ mol H}^+$$

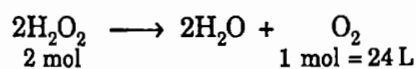
$$= 0.01 \text{ mol HC}_2\text{O}_4^- = y$$

$$\frac{x}{y} = \frac{0.005}{0.01} = \frac{1}{2}$$

$$\therefore y = 2x$$

Hence, (b)

$$11. \quad 100 \text{ mL of } XM \text{ H}_2\text{O}_2 = 0.1 X \text{ mol H}_2\text{O}_2$$



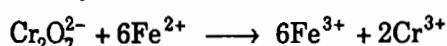
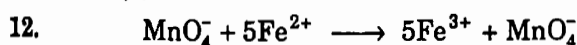
$$24 \text{ L O}_2 = 1 \text{ mol O}_2$$

$$3 \text{ L O}_2 = \frac{1}{8} \text{ mol O}_2 = \frac{1}{4} \text{ mol H}_2\text{O}_2$$

$$0.1 X = \frac{1}{4}$$

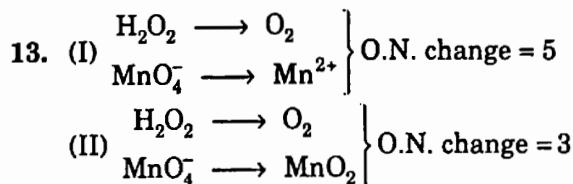
$$\therefore X = 2.5$$

Hence, (a)



$\text{Cr}_2\text{O}_7^{2-}$  oxidises more  $\text{Fe}^{2+}$

Hence, (b)



$$\text{In I:} \quad \begin{array}{cc} \text{(acidic)} & N_1 V_1 = N_2 V_2 \\ & \text{H}_2\text{O}_2 \quad \text{MnO}_4^- \end{array}$$

$$2M_1 \times 100 = 0.5 \times 100$$

$$M_1 (\text{H}_2\text{O}_2) = 2.5 \text{ M}$$

$$\text{In II:} \quad \text{(Basic)} \quad N_1 V_1 = N_2' V_2'$$

$$2M_1 \times 100 = 3 \times M_2 \times V_2'$$

$$2 \times 2.5 \times 100 = 3 \times 1 \times V_2'$$

$$V_2' = \frac{500}{3} \text{ mL}$$

Hence, (b)

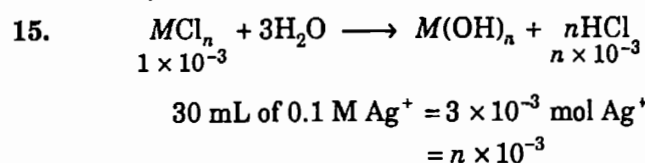
$$14. \quad \text{Normality of "x" volume H}_2\text{O}_2 = \frac{x}{5.6}$$

$$10 \times N_1 (\text{H}_2\text{O}_2) = 10 \times \frac{1}{0.56} (\text{MnO}_4^-)$$

$$N_1 = \frac{1}{0.56} = \frac{x}{5.6}$$

$$\therefore x = 10$$

Hence, (d)



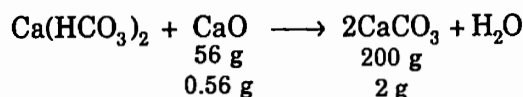
$\therefore n = 3$  thus, trivalent chloride.

Hence, (a)

$$16. \quad \text{Use relation, } M' (\text{molality}) = \frac{1000 M}{(1000 d - Mm)}$$

Hence, (c)

17. Temporary hardness is due to  $\text{HCO}_3^-$  of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$



10 L (=  $10^4$  g) hard water contains = 2 g  $\text{CaCO}_3$

$10^6$  g (ppm) hard water contains = 200 g  $\text{CaCO}_3$

Hence, (b)

$$18. \quad 1 \text{ equivalent of O}_2 = 8 \text{ g} = \frac{1}{4} \text{ mol}$$

Hence, (a)

19.  $\text{SO}_3^{2-}$  is oxidised to  $\text{SO}_4^{2-}$  (change in O.N. = 2)

$$25 \text{ mL of } 0.1 \text{ M SO}_3^{2-} = 2.5 \text{ millimoles}$$

$$= 5.0 \text{ milliequivalents of SO}_3^{2-}$$

$$= 5.0 \text{ milliequivalents of M}^{3+}$$

$$50 \text{ mL of } 0.1 \text{ M M}^{3+} = 5 \text{ millimol (given)}$$

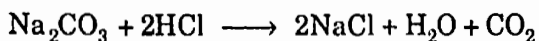
Thus, decrease in O.N. of  $\text{M}^{3+}$  should be 1

So that 5 millimoles = 5 milliequivalents

Thus, new O.N. of  $\text{M}^+ = 2$

Hence, (c)

20. Methyl orange indicates 100% reaction of
- $\text{Na}_2\text{CO}_3$



$$\therefore 20x = 10 \times 0.1 + 5 \times 0.4 = 3$$

$$x = 0.15 \text{ M}$$

Thus, (c)

21. Molality = 9

9 mol  $\text{H}_2\text{SO}_4$  ( $= 9 \times 98 \text{ g H}_2\text{SO}_4$ ) is in 1000 g  $\text{H}_2\text{O}$ Total mass of 9 molal  $\text{H}_2\text{SO}_4$  solution =  $1000 + 98 \times 9$   
= 1882 g1882 g solution has  $\text{H}_2\text{SO}_4 = 882 \text{ g}$ 1000g (= 1 kg) solution has  $\text{H}_2\text{SO}_4 = 469 \text{ g}$ 

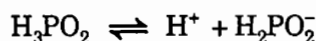
Hence, (b)

22. As in (16)

$$M' = \frac{1000 \times 1}{[1000 \times 1.0585 - 58.5 \times 1]} = 1$$

Hence, (b)

- 23.
- $\text{H}_3\text{PO}_2$
- is monobasic acid



Hence, (a)

- 24.
- $\text{pH} = 2 \therefore [\text{H}^+] = 10^{-2} \text{ M}$

$$[\text{Ca}^{2+}] = \frac{10^{-2}}{2} \text{ M} = \frac{10^{-2}}{2} \text{ mol/L}$$

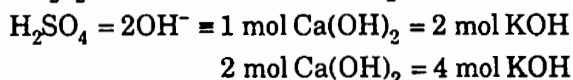
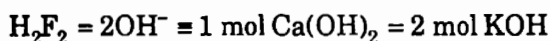
$$= \frac{10^{-2}}{2} \times 40 \text{ g/L}$$

$$= \frac{10^{-2}}{2} \times \frac{40 \times 10^6}{10^3} \text{ ppm}$$

$$= 200 \text{ ppm Ca}^{2+}$$

Hence, (a)

- 25.
- $\text{BaF}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + \text{H}_2\text{F}_2 + \underbrace{\text{H}_2\text{SO}_4}_{\text{unreacted}}$



Hence, (b)

- 26.
- $\text{Na}_2\text{SO}_4$
- remains unreacted

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 100 = (2 \times 0.5) \times 10$$

$$N_1 (\text{NaOH}) = 0.1$$

$$100 \text{ mL of } 0.1 \text{ N NaOH} = 0.01 \text{ mol NaOH}$$

$$= 0.01 \times 40 \text{ g} = 0.4 \text{ g}$$

Hence, (b)

27. 10 mL of
- $x \text{ M NaHC}_2\text{O}_4 \equiv 10 \text{ mL of } 0.1 \text{ M NaOH}$

$$\left\{ \begin{array}{l} \text{H}^+ \text{ ion is neutralised} \\ \therefore x \text{ M} = x \text{ N} \end{array} \right\}$$

$$\therefore 10 \times x = 10 \times 0.1$$

$$x = 0.1 \text{ M}$$

with  $\text{KMnO}_4$ ,  $\text{C}_2\text{O}_4^{2-}$  is oxidised

$$\therefore 0.1 \text{ M} = 0.2 \text{ N H}_2\text{C}_2\text{O}_4$$

$$10 \times 0.2 = 10 \times N' (\text{MnO}_4^-)$$

$$N' = 0.2 \text{ N}$$

 $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$ 

$$\text{Hence, } M(\text{MnO}_4^-) \times 5 = N'$$

$$M(\text{MnO}_4^-) = 0.04 \text{ M}$$

Hence, (c)

28. With phenolphthalein, 50% reaction of
- $\text{Na}_2\text{CO}_3$
- is indicated. With methyl orange, next 50% reaction of
- $\text{Na}_2\text{CO}_3$
- and 100% reaction of
- $\text{NaHCO}_3$
- is indicated.

 $V_1$  = volume of HCl for 100% reaction of  $\text{Na}_2\text{CO}_3$  $V_2$  = volume of HCl for 100% reaction of  $\text{NaHCO}_3$ 

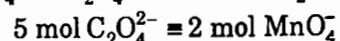
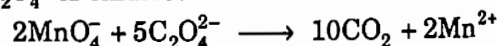
$$\therefore \frac{V_1}{2} = x$$

$$V_2 + \frac{V_1}{2} = y$$

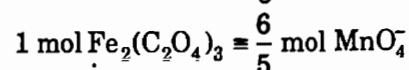
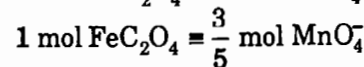
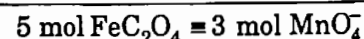
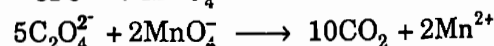
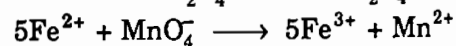
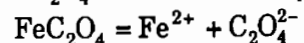
$$\therefore V_2 = (y - x)$$

Hence, (d)

- 29.
- $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \rightleftharpoons 2\text{Fe}^{3+} + 3\text{C}_2\text{O}_4^{2-}$

Only  $\text{C}_2\text{O}_4^{2-}$  is oxidised.

$$\therefore 3 \text{ mol C}_2\text{O}_4^{2-} = 1.2 \text{ mol MnO}_4^-$$

Thus, ratio of  $\text{MnO}_4^-$  required by 1 mol of  $\text{Fe}_2(\text{C}_2\text{O}_4)_3$  and  $\text{FeC}_2\text{O}_4 = 2:1$ 

Hence, (a)

- 30.
- $\text{Na}_2\text{CO}_3$
- and
- $\text{NaHCO}_3$
- are in 1:1 ratio with phenolphthalein 50% reaction of
- $\text{Na}_2\text{CO}_3$
- up to
- $\text{NaHCO}_3$
- is indicated and with methyl orange complete reaction of
- $\text{Na}_2\text{CO}_3$
- and
- $\text{NaHCO}_3$
- is indicated.

$$40 \text{ mL of } 0.05 \text{ M Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$$

$$= 2 \text{ millimoles}$$

$$\text{Na}_2\text{CO}_3 = 1 \text{ millimol}$$

$$\text{NaHCO}_3 = 1 \text{ millimol}$$

 $x \times 0.05$  millimol HCl  $\equiv 0.5$  millimol of  $\text{Na}_2\text{CO}_3$  when 50% of  $\text{Na}_2\text{CO}_3$  (1 millimol) is neutralised

$$y \times 0.05 \text{ millimol HCl} = 2$$

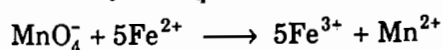
$$\therefore x = 10$$

$$y = 40$$

$$\therefore (y - x) = 30 \text{ mL}$$

Thus, (b)

- 31.
- $\text{MnO}_4^-$
- oxidises only
- $\text{FeSO}_4$

1 mol  $\text{MnO}_4^-$  oxidises = 5 mol  $\text{Fe}^{2+}$  ( $\text{FeSO}_4$ )

$$\frac{100 \times 2}{1000} \text{ mol } \text{MnO}_4^- \text{ oxidises} = 1 \text{ mol } \text{FeSO}_4 \text{ in 3 mol mixture}$$

$$\therefore \text{mole fraction of } \text{FeSO}_4 = \frac{1}{3}$$

Hence, (a)

32. (b) 33. (d)

34. V mL of 1 N unused HCl = 100 mL of 0.5 N NaOH

$$V = 50 \text{ mL}$$

$$\text{Used 1 N HCl} = 100 \text{ mL}$$

$$100 \text{ mL of 1 N HCl} = 0.1 \text{ equivalent HCl}$$

$$= 0.1 \text{ equivalent of } \text{M}_2\text{CO}_3$$

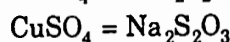
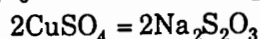
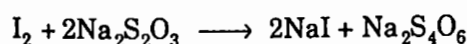
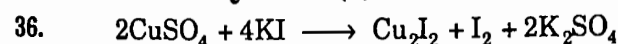
$$\therefore \text{Equivalent mass of } \text{M}_2\text{CO}_3 = \frac{2M + 60}{2} = (M + 30)$$

$$\therefore \frac{5.3}{M + 30} = 0.1$$

$$\therefore M = 23$$

Hence, (a)

35. Proceed as in Q. No. 4. (d)

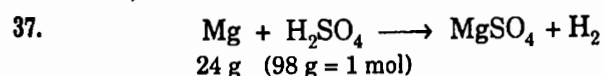


$$100 \text{ mL of 1 M hypo} = 0.1 \text{ mol hypo}$$

$$= 0.1 \text{ mol pure } \text{CuSO}_4$$

Hence, 100% pure

Hence, (a)



$$24 \text{ g } (98 \text{ g} = 1 \text{ mol})$$

$$1.2 \text{ g Mg reacts with} = 0.05 \text{ mol } \text{H}_2\text{SO}_4$$

$$\text{H}_2\text{SO}_4 \text{ taken} = 100 \text{ mL of 1 M } \text{H}_2\text{SO}_4$$

$$= 0.1 \text{ mol}$$

$$\therefore \text{H}_2\text{SO}_4 \text{ left} = 0.1 - 0.05$$

$$= 0.05 \text{ mol in 100 mL solution}$$

$$\therefore [\text{H}_2\text{SO}_4] = 0.05 \times 10 = 0.5 \text{ M}$$

Hence, (a)

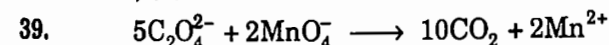
$$38. \quad 10^6 \text{ mL of water has} = 200 \text{ g } \text{CaCO}_3$$

$$10^3 \text{ mL of water has} = 0.200 \text{ g } \text{CaCO}_3$$

$$= 0.002 \text{ mol } \text{CaCO}_3$$

$$\therefore [\text{CaCO}_3] = 0.002 \text{ M}$$

Hence, (b)



$$\text{Also, } 1 \text{ Ca}^{2+} = 1 \text{ C}_2\text{O}_4^{2-}$$

$$20 \text{ mL of } 0.001 \text{ M } \text{MnO}_4^- = 2 \times 10^{-5} \text{ mol } \text{MnO}_4^-$$

$$= 5 \times 10^{-5} \text{ mol } \text{C}_2\text{O}_4^{2-}$$

$$= 5 \times 10^{-5} \text{ mol } \text{Ca}^{2+}$$

$$= 5 \times 10^{-5} \times 40 \text{ g } \text{Ca}^{2+}$$

$$= 0.002 \text{ g } \text{Ca}^{2+}$$

Hence, (d)

- 40.

$$M_1 V_1 = M_2 V_2$$

$$V_1 = \frac{M_2 V_2}{M_1} = \frac{1000 \times 0.9}{18}$$

$$= 50 \text{ mL}$$

Hence, (a)

41. (d)

$$42. \quad 100 \text{ g } \text{H}_3\text{PO}_4 \text{ solution has} = 85 \text{ g } \text{H}_3\text{PO}_4$$

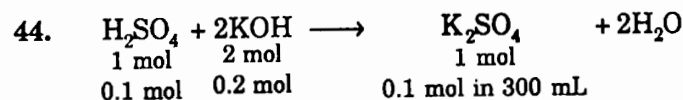
$$\frac{100}{1.7} \text{ mL } \text{H}_3\text{PO}_4 \text{ solution has} = 85 \text{ g } \text{H}_3\text{PO}_4 = \frac{85}{98} \text{ mol}$$

$$\therefore \text{Molarity} = \frac{85/98 \text{ mol}}{\left( \frac{100}{1.7 \times 1000} \text{ L} \right)} = 14.74 \text{ M}$$

Hence, (c)

$$43. \quad M(\text{mixture}) = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2} = 4.125 \text{ M}$$

Hence, (a)



$$\therefore [\text{K}_2\text{SO}_4] = \frac{0.1}{0.3} = 0.333 \text{ M}$$

Hence, (c)

$$45. \quad \text{Molarity} = \frac{\text{"x" volume}}{11.2} = \frac{11.2}{11.2} = 1$$

Hence, (a)

46. (a)

$$47. \quad 0.116 \text{ g } \text{C}_4\text{H}_4\text{O}_4(\text{A}) = \frac{0.116}{116} = 0.001 \text{ mol}$$

$$= 0.001 \times \text{equivalent}$$

$$0.074 \text{ g } \text{Ca}(\text{OH})_2 = \frac{0.074}{74} = 0.001 \text{ mol}$$

$$= 0.002 \text{ equivalent}$$

$$\therefore 0.001x = 0.002$$

$$\therefore x = 2$$

Hence, (b)

$$48. \quad \text{Let } [\text{NaHC}_2\text{O}_4] = x \text{ M}$$

$$= x \text{ N as an acid when } \text{H}^+ \text{ is neutralised}$$

$$= 2x \text{ N as a reducing agent when } \text{C}_2\text{O}_4^{2-} \text{ is oxidised}$$

$$10 \text{ mL of } 2x \text{ NaHC}_2\text{O}_4 = 10 \text{ mL of } 0.02 \text{ M } \text{MnO}_4^-$$

$$= 10 \text{ mL of } 0.1 \text{ N } \text{MnO}_4^-$$

$$\therefore x = 0.05 \text{ M}$$

$$= 0.05 \text{ N}$$

Hence, (b)

$$\text{Sn}^{2+} \text{ taken} = \frac{25 \times 0.05}{1000} = 1.25 \times 10^{-3} \text{ mol}$$

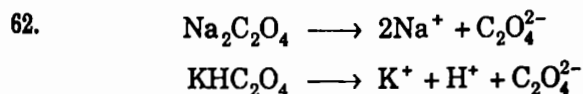
$$\text{Sn}^{2+} \text{ unreacted} = (1.25 \times 10^{-3} - 1.11 \times 10^{-3}) \text{ mol} \\ = 0.14 \times 10^{-3} \text{ mol}$$

$$\therefore \text{Hg}^{2+} \text{ required for oxidising } \text{Sn}^{2+} \\ = 2 \times [\text{Sn}^{2+}] \text{ mol} \\ = 0.28 \times 10^{-3} \text{ mol}$$

Let volume of  $\text{HgCl}_2 = V \text{ mL}$

$$\therefore \frac{V \times 0.05}{1000} = 0.28 \times 10^{-3} \\ = 5.6 \text{ mL}$$

Hence, (c)



$$\text{Let} \quad \text{Na}_2\text{C}_2\text{O}_4 = x \text{ mol} \\ \text{KHC}_2\text{O}_4 = y \text{ mol}$$

$$\text{Then } \text{C}_2\text{O}_4^{2-} = (x + y) \text{ mol} = 2(x + y) \text{ equivalents}$$

$$\text{H}^+ = y \text{ mol} = y \text{ equivalents}$$

Let volume of 0.1 N base required =  $V \text{ mL}$

$$\text{Then} \quad \frac{0.1 \times V}{1000} = y$$

$$\therefore V = 10000 y$$

$$\text{Volume of 0.1 N KMnO}_4 = 3 V$$

$$\therefore \frac{0.1 \times 3 V}{1000} = 2(x + y)$$

$$\frac{0.1 \times 3 \times 10000 y}{1000} = 2(x + y)$$

$$3y = 2x + 2y$$

$$\therefore y = 2x$$

$$\therefore \text{Na}_2\text{C}_2\text{O}_4 = 134 x \text{ g}$$

$$\text{KHC}_2\text{O}_4 = y = 2x \text{ mol} = 2x \times 128 \text{ g} = 256x \text{ g}$$

$$\therefore \% \text{ of KHC}_2\text{O}_4 = \frac{256x \times 100}{256x + 134x} \\ = 65.64\%$$

Hence, (a)

63. Since,  $40.38 \text{ mL} > 12.83 \text{ mL}$ , the sample must contain NaOH and  $\text{Na}_2\text{CO}_3$ .

Hence, (b)

64. The volume of titrant used by  $\text{Na}_2\text{CO}_3$  in the second step =  $12.83 \text{ mL}$ .

Thus, volume of HCl used by NaOH in first step

$$= 40.38 - 12.83$$

$$= 27.55 \text{ mL}$$

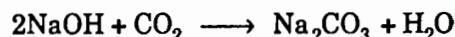
$$\therefore \% \text{ of NaOH} = \frac{27.55 \times 0.1062 \times 40 \times 100}{1000 \times 0.6234}$$

$$= 18.77$$

Hence, (a)

$$65. \text{ Moles of NaOH initially} = \frac{200 \times 0.100}{1000} = 0.02 \text{ mol}$$

$$\text{CO}_2 \text{ absorbed} = 1 \text{ millimol} = 0.001 \text{ mol}$$



$$\text{Thus, NaOH reacted} = 0.001 \times 2 = 0.002 \text{ mol}$$

$$\text{Na}_2\text{CO}_3 \text{ formed} = 0.001 \text{ mol}$$

$$\text{NaOH unreacted} = 0.02 - 0.002 = 0.018 \text{ mol}$$

Thus, HCl required by NaOH for phenolphthalein end point

$$= 0.018 \text{ mol}$$

$$\text{Equivalent of Na}_2\text{CO}_3 = 0.002 \text{ equivalents}$$

$\therefore$  Moles of HCl required by 0.002 equivalents for

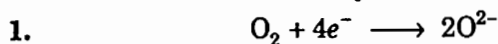
$$\text{phenolphthalein end point} = \frac{0.002}{2} = 0.001 \text{ (50\% reaction is indicated upto NaHCO}_3\text{)}$$

$$\therefore \text{Total HCl} = (0.018 + 0.001) \text{ mol in } 200 \text{ mL}$$

$$\therefore N(\text{HCl}) = \frac{(0.018 + 0.001)}{0.2} \text{ mol L}^{-1} \\ = 0.095 \text{ M} \\ = 0.095 \text{ N}$$

Hence, (c)

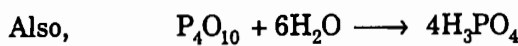
### One or More Than One Options Correct



$$4e^- \equiv 1 \text{ mol O}_2 = 0.25 \text{ mol} = 8 \text{ g O}_2$$

Thus, (a) and (b) correct

$$2. \quad 2.84 \text{ g P}_4\text{O}_{10} = \frac{2.84}{284} = 0.01 \text{ mol L}^{-1} \text{ P}_4\text{O}_{10}$$



$$\text{Thus, } 0.01 \text{ M P}_4\text{O}_{10} = 0.01 \times 4 \text{ M H}_3\text{PO}_4 \\ = 0.04 \text{ M H}_3\text{PO}_4$$

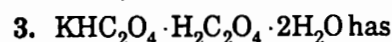
$$1 \text{ L of } 0.04 \text{ M H}_3\text{PO}_4 \equiv 1 \text{ L of } 0.12 \text{ N H}_3\text{PO}_4$$

$$\equiv 1 \text{ L of } 0.12 \text{ N NaOH}$$

$$\equiv 400 \text{ mL of } 0.3 \text{ N NaOH (to Na}_3\text{PO}_4 \text{ stage)}$$

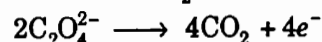
$$\equiv 400 \text{ mL of } 0.1 \text{ M (= 0.2 N) Ca(OH)}_2 \text{ (to CaHPO}_4\text{)}$$

Thus, (b) and (c) are true



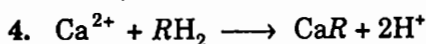
$$(i) \text{ three ionisable H}^+. \text{ If it is } 0.2 \text{ N then it is} \\ = \frac{0.2}{3} \text{ M} = 0.067 \text{ M}$$

$$(ii) \text{ two } \text{C}_2\text{O}_4^{2-} \text{ oxidised to } \text{CO}_2$$



$$\text{Thus, } 0.067 \text{ M} = 0.067 \times 4 = 0.267 \text{ N}$$

Thus, (a) and (c) are true.



$$77.5 \text{ ppm} = 77.5 \text{ g Ca}^{2+} \text{ per } 10^6 \text{ mL}$$

$$= 77.5 \times 10^{-3} \text{ g L}^{-1} \text{ Ca}^{2+}$$

$$= \frac{77.5 \times 10^{-3}}{40} \text{ mol L}^{-1} \text{ Ca}^{2+} \text{ ion}$$

$$= \frac{77.5 \times 10^{-3} \times 2}{40} \text{ mol L}^{-1} \text{ H}^+ \text{ ion}$$

$$\therefore [\text{H}^+] = 3.875 \times 10^{-3}$$

$$\therefore \text{pH} = -\log(\text{H}^+) = 2.4$$

Thus, (a) and (c) are true.



$$5. \quad 10.78 \text{ g H}_3\text{PO}_4 \text{ is } 0.550 \text{ L} = \frac{10.78/98}{0.550} = 0.2 \text{ M}$$

But it is 0.4 N hence

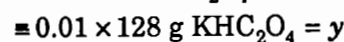
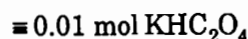
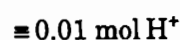
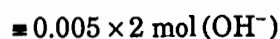
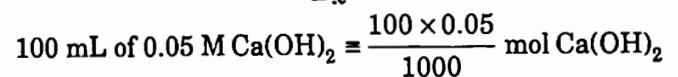
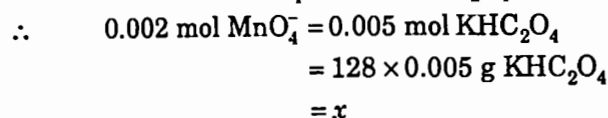
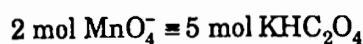
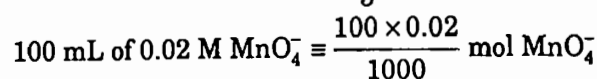
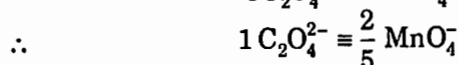
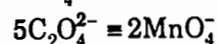
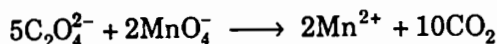
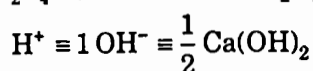
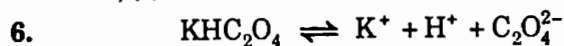
$\text{H}_3\text{PO}_4$  has been changed to  $\text{HPO}_4^{2-}$  (by neutralisation of  $2\text{H}^+$ ). Thus, (a) is true.

When  $\text{H}_3\text{PO}_4$  (O.N. of P = +5) is reduced to  $\text{HPO}_3^{2-}$  (O.N. of P = +3)

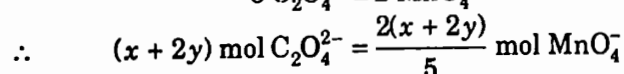
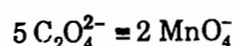
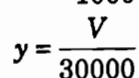
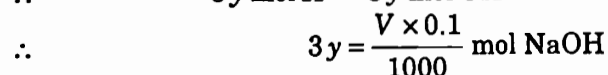
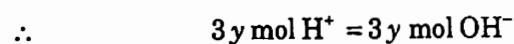
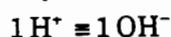
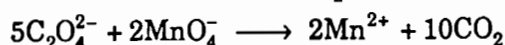
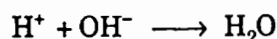
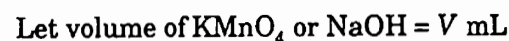
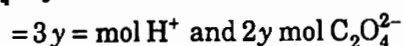
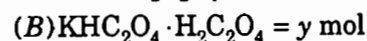
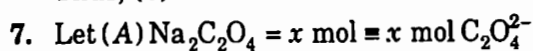
Change in O.N. = 2 units

Thus,  $0.2 \text{ M} = 0.4 \text{ N}$

Then, (c) is also true. Thus, (a) and (c)



Thus, (b)



$$\therefore \frac{2(x + 2y)}{5} = \frac{V \times 0.1}{1000} \text{ mol KMnO}_4$$

$$(x + 2y) = \frac{5V}{20000}$$

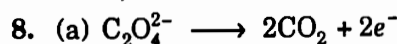
$$\frac{x + 2y}{y} = \frac{5 \times 3}{2} = 7.5$$

$$\frac{x}{y} + 2 = 7.5$$

$$\frac{x}{y} = 5.5$$

Thus,  $x : y = 5.5 : 1$

Thus, (c)



$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{2}$$

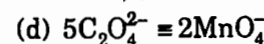
Thus, (a) is not true.

(b)  $\text{H}_2\text{C}_2\text{O}_4$  has  $2\text{H}^+$  ions while  $\text{NaHC}_2\text{O}_4$  has  $1\text{H}^+$  ion

Thus, (b) is not true

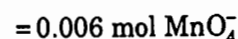
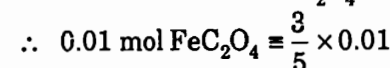
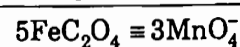
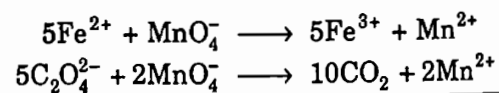
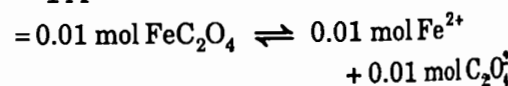
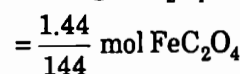
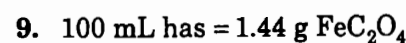
(c) Equivalent of  $\text{H}_2\text{C}_2\text{O}_4 \equiv \text{NaHC}_2\text{O}_4$

Thus, (c) is true



Thus, (d) is also true.

Thus, (c) and (d)

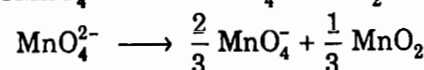
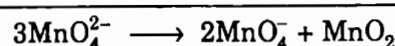
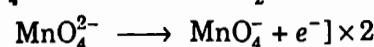
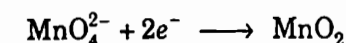
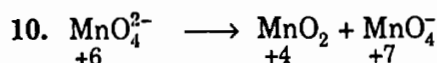


Let volume of  $\text{KMnO}_4 = V \text{ mL}$

$$\therefore \frac{V \times 0.01}{1000} = 0.006$$

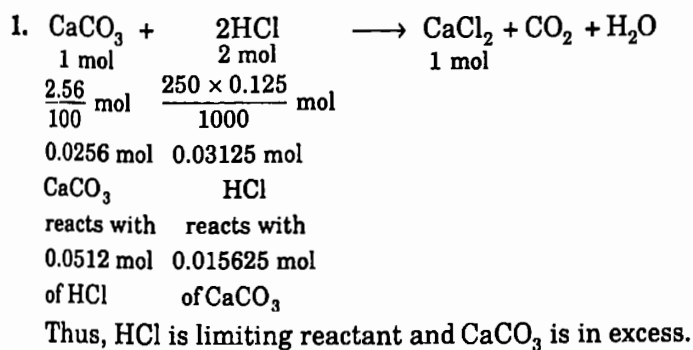
$$V = \frac{0.006 \times 1000}{0.01} = 600 \text{ mL}$$

Thus, (b)



Thus, (a)

## Brain Twisters



$$\text{CaCO}_3 \text{ left unreacted} = 0.0256 - 0.0156$$

$$= 0.01 \text{ mol}$$

$$= 1.0 \text{ g}$$

$$\text{CaCl}_2 \text{ formed} = \text{moles of CaCO}_3 \text{ reacted}$$

$$= 0.015625 \text{ mol} = 1.7344 \text{ g}$$

2. (a) Oxidising agent :  $\text{O}_2$ , oxidises Au

Reducing agent : Au, reduces  $\text{O}_2$

(b) Gold = 1000 kg impure

$$= 1000 \times 1000 \times \frac{0.0197}{100} \text{ g pure}$$

$$= 197 \text{ g}$$

$$= 1 \text{ mol}$$

$$\text{Moles of NaCN} = V (\text{litres required}) \times M$$

$$= 0.075 V$$

$$4 \text{ mol Au require} = 8 \text{ mol NaCN}$$

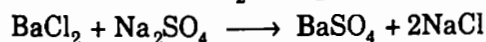
3. 1 mol Au requires = 2 mol NaCN

$$\therefore 0.075 V = 2$$

$$V = 26.67 \text{ L}$$

$$500 \text{ mL of } 0.25 \text{ mol Na}_2\text{SO}_4 = 0.125 \text{ mol}$$

$$\text{BaCl}_2 = 15 \text{ g} = 0.0721 \text{ mol}$$



Thus,  $\text{BaCl}_2$  is limiting reactant

$$\text{BaCl}_2 = \text{BaSO}_4 = 0.0721 \text{ mol}$$

4. NaCl and HCl are strong electrolytes thus, ionise completely in aqueous solution.

$$p_{\text{Na}^+} = -\log 2 \times 10^{-3}$$

$$= 3 - \log 2$$

$$= 3 - 0.3010 = 2.6990$$

$$p_{\text{H}^+} = -\log 5.4 \times 10^{-4}$$

$$= 4 - \log 5.4$$

$$= 4 - 0.7324$$

$$= 3.2676$$

$$\text{Total } [\text{Cl}^-] = 2 \times 10^{-3} + 5.4 \times 10^{-4}$$

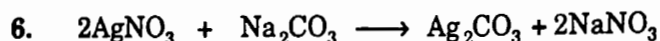
$$= 2.54 \times 10^{-3} \text{ M}$$

$$p_{(\text{Cl}^-)} = 2.595$$

$$5. \quad p_{\text{Ag}^+} = 6.6990$$

$$[\text{Ag}^+] = 10^{-6.6990} = 10^{-7} 10^{0.3010}$$

$$= 2 \times 10^{-7}$$



$$2 \text{ mol} : 1 \text{ mol} \quad 1 \text{ mol}$$

$$25.0 \text{ mol of} : 50.0 \text{ mol of}$$

$$0.2 \text{ M} : 0.08 \text{ M}$$

$$0.005 \text{ mol} : 0.004 \text{ mol}$$

will react with : will react

$$0.0025 \text{ mol of} : \text{with } 0.008 \text{ mol}$$

$$\text{Na}_2\text{CO}_3 : \text{of AgNO}_3$$

Thus,  $\text{AgNO}_3$  is limiting reactant

$$\text{Thus, Ag}_2\text{CO}_3 \text{ formed} = \frac{1}{2} \text{ mol of AgNO}_3$$

$$= 0.0025 \text{ mol}$$

$$= 0.0025 \times 276 = 0.69 \text{ g}$$

7. In the above case  $\text{Na}_2\text{CO}_3$  left unreacted

$$= 0.004 - 0.0025$$

$$= 0.0015 \text{ mol in total } 75 \text{ mL}$$

$$= (0.075 \text{ L})$$

$$\text{Thus, molar concentration of Na}_2\text{CO}_3 = \frac{0.0015 \text{ mol}}{0.075 \text{ L}}$$

$$= 0.02 \text{ M}$$

$$8. \quad (a) \quad [\text{Cu}^{2+}] = 4.78 \times 10^{-2}$$

$$\therefore p_{\text{Cu}^{2+}} = -\log [\text{Cu}^{2+}]$$

$$= -\log 4.78 \times 10^{-2}$$

$$= 2 - \log 4.78$$

$$= 2 - 0.6794$$

$$= 1.3206$$

$$[\text{Zn}^{2+}] = 0.104 = 1.04 \times 10^{-1}$$

$$p_{\text{Zn}^{2+}} = -\log [\text{Zn}^{2+}]$$

$$= -\log 1.04 \times 10^{-1}$$

$$= 1 - \log 1.04$$

$$= 1 - 0.0170$$

$$= 0.9830$$

$$[\text{NO}_3^-] = 2 \times 4.78 \times 10^{-2} [\text{from Cu(NO}_3)_2]$$

$$+ 2 \times 0.104 [\text{from Zn(NO}_3)_2]$$

$$= 2.1756 \times 10^{-1}$$

$$\therefore p_{\text{NO}_3^-} = -\log [\text{NO}_3^-]$$

$$= -\log (2.1756 \times 10^{-1})$$

$$= 1 - \log 2.1756$$

$$= 1 - 0.3376$$

$$= 0.6624$$

$$(b) \quad [\text{H}^+] = 6.75 \times 10^{-4}$$

$$\therefore p_{\text{H}^+} = -\log [\text{H}^+]$$

$$= -\log 6.75 \times 10^{-4}$$

$$= 3.1707$$

$$[\text{Ba}^{2+}] = 3.35 \times 10^{-4}$$

$$\therefore p_{\text{Ba}^{2+}} = -\log 3.35 \times 10^{-4}$$

$$= 3.4750$$

$$\begin{aligned}
 [\text{ClO}_4^-] &= 2 \times 3.35 \times 10^{-4} \text{ from Ba}(\text{ClO}_4)_2 \\
 &\quad + 6.75 \times 10^{-4} \text{ from HClO}_4 \\
 &= 13.45 \times 10^{-4} \text{ M} \\
 p_{\text{ClO}_4^-} &= -\log 13.45 \times 10^{-4} \\
 &= 2.8713
 \end{aligned}$$

9. (a)  $\text{Na}^+ = 1.08 \times 10^{-3} \text{ ppm}$

Thus,  $10^6 \text{ g}$  of sea water has  $= 1.08 \times 10^3 \text{ g Na}^+$

$\frac{10^6}{1.02} \text{ mL}$  of sea water has  $= 1.08 \times 10^3 \text{ g Na}^+$

$\therefore 10^3 \text{ mL}$  of sea water has

$$= \frac{1.08 \times 10^3 \times 1.02 \times 10^3}{10^6} \text{ g Na}^+$$

$$= 1.1016 \text{ g L}^{-1}$$

$$= 4.8 \times 10^{-2} \text{ M}$$

$\therefore$  Similarly  $[\text{SO}_4^{2-}] = \frac{270 \times 1.02 \times 10^3}{10^6} = 0.2754 \text{ g L}^{-1}$

$$= 2.87 \times 10^{-3} \text{ M}$$

(b)  $p_{\text{Na}^+} = 1.32$

$$p_{\text{SO}_4^{2-}} = 2.54$$

10.  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O} = 5.76 \text{ g}$  in  $2 \text{ L}$  solution

$$= \frac{5.76}{277.5} \text{ mol in } 2 \text{ L solution}$$

$$= 0.01 \text{ M}$$

(a)  $[\text{KCl} \cdot \text{MgCl}_2] = 0.01 \text{ M}$

(b)  $[\text{Mg}^{2+}] = 0.01 \text{ M}$

$$[\text{Cl}^-] = 0.03 \text{ M}$$

(c) Millimoles of  $\text{Cl}^-$  in  $25.0 \text{ mL}$  solution

$$= 0.03 \times 25 = 0.75$$

(d)  $[\text{K}^+] = 0.01 \text{ M}$

$$= 0.39 \text{ g L}^{-1}$$

$$= \frac{0.39}{1000} \times 10^6 \text{ g per million}$$

$$= 390 \text{ ppm}$$

11.  $\text{KI} = 24.32 \text{ ppt}$

$$= 24.32 \text{ g per thousand mL solution}$$

$$= \frac{24.32}{1000} \times 200 \text{ g in } 200 \text{ mL solution}$$

$$= 4.864 \text{ g}$$

$$= 0.038 \text{ mol}$$

Volume of  $\text{AgNO}_3$  required  $= V \text{ mL}$

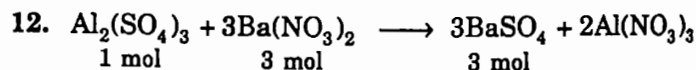
$$\text{Molarity} = 0.01 \text{ M}$$

$\therefore 0.01 \text{ M} \times V = 0.01 V \text{ millimol}$

$$= 1 \times 10^{-5} V \text{ mol}$$

$$1 \times 10^{-5} V = 0.038$$

$$V = \frac{0.038}{1 \times 10^{-5}} = 3800 \text{ mL}$$



$$\text{Ba}(\text{NO}_3)_2 = 480.4 \text{ ppm (parts per million)}$$

$$= 480.4 \text{ g in } 10^6 \text{ mL}$$

$$= \frac{480.4 \times 750}{10^6} \text{ g in } 750 \text{ mL}$$

$$= 0.3603 \text{ g}$$

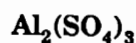
$$= \frac{0.3603}{261}$$

$$= 1.3804 \times 10^{-3} \text{ mol}$$

$$\text{Al}_2(\text{SO}_4)_3 = 200 \times 0.03090 \text{ millimol}$$

$$= 6.18 \text{ millimol}$$

$$= 6.18 \times 10^{-3} \text{ mol}$$



$$\text{Ba}(\text{NO}_3)_2 = \frac{1}{3} \text{ based on stoichiometry}$$

$$= \frac{6.18 \times 10^{-3}}{1.3804 \times 10^{-3}} = 4.5$$

Thus,  $\text{Ba}(\text{NO}_3)_2$  is limiting reactant and  $\text{Al}_2(\text{SO}_4)_3$  is in excess.

(a) Thus  $\text{BaSO}_4$  formed  $= 1.3804 \times 10^{-3} \text{ mol}$

$$= 1.3804 \times 10^{-3} \times 233 \text{ g}$$

$$= 0.3216 \text{ g}$$

(b) Unreacted  $\text{Al}_2(\text{SO}_4)_3 = 6.18 \times 10^{-3} - \frac{1.3804 \times 10^{-3}}{3}$

$$= 5.72 \times 10^{-3} \text{ mol in } 950 \text{ mL}$$

$$= 6.02 \times 10^{-3} \text{ M}$$

13. Let unreacted  $\text{AgNO}_3$  be  $= V \text{ mL}$

$$V \text{ mL of } 0.082 \text{ M AgNO}_3 = 4.86 \text{ mL of } 0.0625 \text{ M KSCN}$$

$$\therefore V = \frac{4.86 \times 0.0625}{0.082}$$

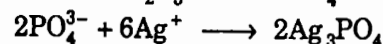
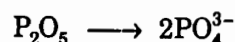
$$= 3.70 \text{ mL}$$

$\therefore$  used  $\text{AgNO}_3 = (50.0 - 37.0) \text{ mL}$

$$= 13.0 \text{ mL}$$

$$\text{Moles of AgNO}_3 \text{ used} = \frac{13.0 \times 0.082}{1000}$$

$$= 1.066 \times 10^{-3} \text{ mol}$$



$$\text{Thus, P}_2\text{O}_5 \text{ content} = \frac{1.066 \times 10^{-3}}{6} \text{ mol}$$

$$= 1.777 \times 10^{-4} \text{ mol}$$

$$= \frac{1.777 \times 10^{-4}}{6} \times 142 \text{ g}$$

$$= 0.00417 \text{ g}$$

$$\text{Thus, \% of P}_2\text{O}_5 \text{ in plant food} = \frac{0.00417}{4.258} \times 100$$

$$= 0.098\%$$

14.  $0.30 \text{ M CaCl}_2 = 0.60 \text{ M Cl}^-$  (in  $\text{CaCl}_2$ )

$$\text{Volume of CaCl}_2 = V_1 \text{ mL}$$

$$\text{KCl} = 0.20 \text{ M} = 0.20 \text{ M Cl}^-$$

Volume of KCl solution = 400 mL

Resultant molarity of  $\text{Cl}^- = 0.25 \text{ M}$

$$\text{Resultant molarity} = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$$

$$0.25 = \frac{0.60 V_1 + 0.20 \times 400}{V_1 + 400}$$

$$V_1 = 57.14 \text{ mL}$$

15. 60 L of 0.50 NaOH  $\equiv 60 \times 0.5 \text{ mol NaOH}$  if pure

$= 30 \text{ mol NaOH}$  if pure

$= 30 \times 40 \text{ g NaOH}$  if pure

$$= \frac{30 \times 40 \times 100}{88} \text{ g NaOH if wet}$$

$$= 1363.64 \text{ g}$$

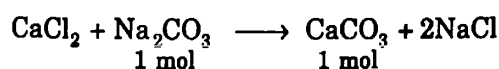
16. 50 mL of  $N_1 \text{ Na}_2\text{CO}_3 \equiv 56.3 \text{ mL}$  of 0.102 N HCl

$$\therefore 50 \times N_1 = 56.3 \times 0.102$$

$$N_1 = 0.115 \text{ N Na}_2\text{CO}_3$$

$$= 0.0575 \text{ M Na}_2\text{CO}_3$$

$\therefore 100 \text{ mL}$  of 0.0575 M  $\text{Na}_2\text{CO}_3 = 5.75 \times 10^{-3} \text{ mol}$



$$5.75 \times 10^{-3} \text{ mol} \quad 5.75 \times 10^{-3} \text{ mol}$$

$$\text{CaCO}_3 \text{ formed} = 5.75 \times 10^{-3} \text{ mol}$$

$$= 5.75 \times 10^{-3} \times 100 \text{ g}$$

$$= 0.575 \text{ g}$$

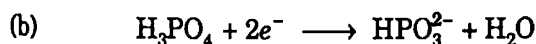
17. (a) If  $\text{H}_3\text{PO}_4$  is completely neutralised then it behaves as a tribasic acid thus,  $0.40 \text{ N H}_3\text{PO}_4 = \frac{0.40 \text{ M}}{3} \text{ H}_3\text{PO}_4$

$$\text{Moles in one litre} = \frac{0.40}{3} \text{ mol}$$

$$\therefore \text{Moles in 550 mL} = \frac{0.40 \times 550}{3 \times 1000}$$

$$\text{Amount of H}_3\text{PO}_4 = \frac{0.40 \times 550 \times 98}{3 \times 1000} \text{ g}$$

$$= 7.187 \text{ g}$$



Due to reduction as a result of gain of two electrons.

$$0.40 \text{ N H}_3\text{PO}_4 = \frac{0.40 \text{ M}}{2} \text{ H}_3\text{PO}_4$$

Moles of  $\text{H}_3\text{PO}_4$  in one litre = 0.20 mol

$$\text{Moles in 550 mL} = \frac{0.20 \times 550}{1000}$$

$$\text{Amount of H}_3\text{PO}_4 = \frac{0.20 \times 550 \times 98}{1000} \text{ g}$$

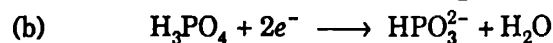
$$= 10.78 \text{ g}$$

Alternate (short method)



$$\text{Equivalent weight of H}_3\text{PO}_4 = \frac{98}{3}$$

$$\therefore w(\text{amount}) = \frac{NEV}{1000} = \frac{0.40 \times 98 \times 550}{1000 \times 3} = 7.187 \text{ g}$$



$$\text{Equivalent weight of H}_3\text{PO}_4 = \frac{98}{2} = 49$$

$$\therefore w(\text{amount}) = \frac{NEV}{1000} = \frac{0.40 \times 49 \times 550}{1000} = 10.78 \text{ g}$$

## Passage Comprehension Questions

### Passage 1

$$\text{Molar mass of Cr(NH}_3)_x\text{Cl}_3 = 52 + 17x + 35.5 \times 3 = (158.5 + 17x)$$

$\text{NH}_3$  in the complex is neutralised by HCl.

$$\text{Moles of HCl required} = \frac{40 \times 1.5}{1000} = 0.06$$

$$\text{Moles of A} = \frac{2.635}{(158.5 + 17x)}$$

$$\text{Thus, } \frac{0.06}{x} = \frac{2.635}{(158.5 + 17x)}$$

$$\therefore x = 5.89 \approx 6$$

1. Thus,  $x = 6$ , Thus (d)

2. 1.5 M  $\text{H}_2\text{SO}_4$  being dibasic, volume of  $\text{H}_2\text{SO}_4$  required will be = 20 mL

Thus, (b)

3. Thus, complex is  $(\text{Cr(NH}_3)_6)\text{Cl}_3$

Thus, (a)

### Passage 2

1. (c)    2. (a)    3. (d)    4. (b), (d)

### Passage 3

$$\text{A. Resultant molarity of HCl} = \frac{20 \times 1}{40}$$

due to dilution from 20 mL to 40 mL = 0.5 M

Thus, 40 mL of 0.5 M HCl  $\equiv V_A \text{ mL}$  of 0.1 M NaOH

$$\therefore V_A = 200 \text{ mL}$$

$$\text{B. Resultant molarity of HCl due to dilution from 20 mL to 80 mL} = \frac{20 \times 1}{80}$$

$$= 0.25 \text{ M}$$

Thus, 80 mL of 0.25 M HCl  $\equiv V_B \text{ mL}$  of 0.1 M

$$V_B = 200 \text{ mL}$$

1. Thus,  $V_A = V_B$ , Thus, (a)

2. (b)

3. At the end-point additional drop of NaOH, imparts pink colour.

Thus, (c)

#### Passage 4

| $\text{MnO}_4^- \xrightarrow{\text{H}^+} \text{Mn}^{2+}$ | Change in O.N. | Volume of $\text{KMnO}_4$ |
|----------------------------------------------------------|----------------|---------------------------|
| +7                                                       | +2             | 5 unit                    |
| $\xrightarrow{\text{OH}^-} \text{Mn}^{x+}$               | (7 - x) unit   | $V_A$ 20 mL               |
| $\xrightarrow{\text{neutral}} \text{Mn}^{y+}$            | (7 - y) unit   | $V_B$ 33.4 mL             |
|                                                          |                | $V_C$ 100 mL              |

1 M  $\text{MnO}_4^- = 5 \text{ N}$  in acidic medium

$= (7 - x) \text{ N}$  in basic medium

$= (7 - y) \text{ N}$  in neutral medium

20 mL of 5 N  $\text{MnO}_4^- = 33.4 \text{ mL}$  of  $(7 - x) \text{ N}$   $\text{MnO}_4^-$

$$\frac{100}{33.4} = 7 - x$$

$$x = 4$$

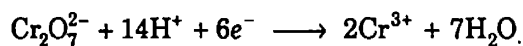
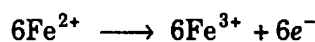
Also, 20 mL of 5 N  $\text{MnO}_4^- = 100 \text{ mL}$  of  $(7 - y) \text{ N}$   $\text{MnO}_4^-$

$$\therefore (7 - y) = 1$$

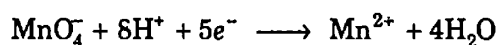
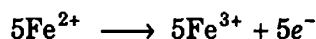
$$y = 6$$

1. (a)    2. (c)    3. (b)

#### Passage 5



$$N(\text{Cr}_2\text{O}_7^{2-}) = 6 \times M(\text{Cr}_2\text{O}_7^{2-}) \\ = 0.6 \text{ N}$$



$$N(\text{MnO}_4^-) = 5 \times M(\text{MnO}_4^-) \\ = 0.5 \text{ N}$$

Volume of  $\text{Fe}^{2+} = V \text{ mL}$  (say)

Molarity of  $\text{Fe}^{2+} = 1 \text{ M}$  (say)  $= 1 \text{ N}$

$$1. \quad 6\text{Fe}^{2+} \equiv \text{Cr}_2\text{O}_7^{2-}$$

$$1 \text{ Fe}^{2+} \equiv \frac{\text{Cr}_2\text{O}_7^{2-}}{6}$$

$$5 \text{ Fe}^{2+} \equiv \text{MnO}_4^-$$

$$1 \text{ Fe}^{2+} \equiv \frac{\text{MnO}_4^-}{5}$$

In all cases

1 equivalent of X  $\equiv$  1 equivalent of Y

Thus, (d)

$$2. \quad \begin{aligned} V \times 1 &\equiv 0.5 \times V_1 && \text{for } \text{MnO}_4^- \\ V_1 &= 2V \\ V \times 1 &\equiv 0.6 \times V_2 && \text{for } \text{Cr}_2\text{O}_7^{2-} \\ V_2 &= 1.33V \end{aligned}$$

Thus, (b)

$$3. \quad 24.5 \text{ mL of } 0.1 \text{ M } \text{Cr}_2\text{O}_7^{2-} \equiv 24.5 \text{ mL of } 0.6 \text{ N } \text{Cr}_2\text{O}_7^{2-}$$

$$V \text{ mL of } 0.1 \text{ M } \text{MnO}_4^- = V \text{ mL of } 0.5 \text{ N } \text{MnO}_4^-$$

$$\text{Thus, } 24.5 \times 0.6 \equiv V \times 0.5$$

$$\therefore V = 29.4 \text{ mL}$$

Thus, (a)

#### Passage 6

$$\begin{aligned} 1. \quad (c) \quad 25 \text{ mL of } 1 \times 10^{-3} \text{ M } \text{MnO}_4^- \\ &\equiv 25 \text{ mL of } 5 \times 10^{-3} \text{ N } \text{MnO}_4^- \\ &\equiv 0.125 \text{ milliequivalent of } \text{MnO}_4^- \\ &\equiv 0.125 \text{ milliequivalent of } \text{CaC}_2\text{O}_4 \\ &\equiv 0.125 \text{ milliequivalent of } \text{Ca}^{2+} \\ &\equiv 0.125 \times 20 \text{ mg of } \text{Ca}^{2+} \text{ in } 10 \text{ mL} \\ &\equiv 0.250 \text{ mg/mL } \text{Ca}^{2+} \text{ solution} \end{aligned}$$

2. (a) Explained above

$$3. \quad (a) \quad 0.250 \text{ mg/mL} = 0.250 \text{ g/L} \\ = 250 \text{ g}/10^6 \text{ mL} = 250 \text{ ppm}$$

4. (c) In  $\text{H}_2\text{SO}_4$ , HCl, it is decomposed.

$\text{HCOOH}$  is oxidised by  $\text{KMnO}_4$ , hence cannot be used.

5. (d)

#### Passage 7

1. (c) Only  $\text{Fe}^{2+}$  is oxidised and  $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$

$$25 \times M(\text{Fe}^{2+}) = 25 \times 0.02 \times 5 (\text{MnO}_4^-)$$

$$M = 0.10 \text{ M}$$

2. (a) Total  $\text{Fe}^{2+}$  in second part (including that of from  $\text{Fe}^{3+}$ )

$$25 \times y = 40 \times 0.02 \times 5$$

$$y = 0.16 \text{ M} = 0.16 \text{ N}$$

$$\therefore \text{Fe}^{3+} = 0.16 - 0.10 (\text{Fe}^{2+}) = 0.06 \text{ M}$$

3. (b)

$$4. \quad (c) \quad 25 \text{ mL of } 0.10 \text{ M } \text{Fe}^{2+} = V_1 \text{ mL of } 0.02 \text{ M } \text{K}_2\text{Cr}_2\text{O}_7$$

$$= V_1 \times 0.02 \times 6 \text{ N } \text{K}_2\text{Cr}_2\text{O}_7$$

$$V_1 = 20.83 \text{ mL}$$

( $\text{Cr}_2\text{O}_7^{2-}$  is reduced to  $\text{Cr}^{3+}$ )

Similarly for 0.16 ( $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ )

$$V_2 = 33.33 \text{ mL}$$

#### Passage 8

$$1. \quad (c) \quad 5.8 \text{ g } \text{NaIO}_3 = \frac{5.8}{198} \text{ mol } \text{NaIO}_3$$

$$\text{NaHSO}_3 = \frac{3 \times 5.8}{198} \text{ mol}$$

$$= \frac{3 \times 5.8 \times 104}{198} \text{ g} = 9.14 \text{ g}$$

$$2. \quad (a) \quad \text{I}^- \text{ formed in step I} = \frac{5.8}{198} \text{ mol}$$

$$\text{IO}_3^- \text{ required in step II} = \frac{5.8}{198 \times 5} \text{ mol} = 1.16 \text{ g } (\text{NaIO}_3)$$

$$\text{volume} = \frac{1.16}{5.8} = 0.2 \text{ L}$$

|   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 6 | 2 | 1 | 7 | 1 | 3 | 2 | 2 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
| 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
| 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
| 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |



There is nothing in the universe but alkali and acid, from which nature composes all things.

O. Tachenius

# 8

## s-Block Elements —The Alkali Metals

### Quick Points

- Effective nuclear charge  $Z^*$  (due to shielding effect)

$$Z^* = Z - S$$

where  $Z$  is atomic number and

$S$  is the shielding constant

Value of  $Z^*$  is derived by using Slater's rule;

$S = 0.25$  for 1s-electron when it is alone (only for He)

$= 0.35$  per electron in  $n^{\text{th}}$  orbit

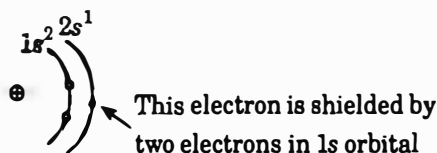
$= 0.85$  per electron in  $(n-1)^{\text{th}}$  orbit

$= 1.00$  per electron in  $(n-2), (n-3) \dots$  orbit

Thus, for Li ( $Z = 3, 1s^2 2s^1$ )

$Z^* = 3 -$  shielding constant of two electrons in 1s  
-suborbit  $(n-1)^{\text{th}}$  orbit

$$= 3 - 2 \times 0.85 = 1.30$$



For second period,  $Z^* = 0.65(n+1)$

where  $n$  is the number of valence electrons.

For Na ( $Z = 11, 1s^2 2s^2 2p^6 3s^1$ )

Electron in 3s-suborbit is shielded by 8 electrons in 2nd, i.e.,  $(n-1)^{\text{th}}$  orbit and 2 electrons in 1st, i.e.,  $(n-2)^{\text{th}}$  orbit

Thus,  $S = 8 \times 0.25 + 2 \times 1 = 8.8$

$$\therefore Z^* = 11 - 8.8 = 2.2$$

- Species with N-unpaired electrons is paramagnetic and magnetic moment  $= \sqrt{N(N+2)}$  BM

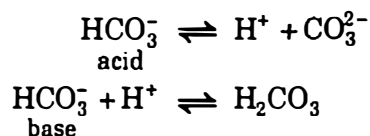
### Learning Framework of the Chapter

- Introduction
- Periodicity at a Glance
- Study of Group 1 (IA)  
— The Alkali Metals
- Compounds of Sodium
- Compounds of Potassium
- Diagonal Relationship
- Anomalous Behaviour of Lithium
- Additional Reactions and Facts of Alkali Metals 1A

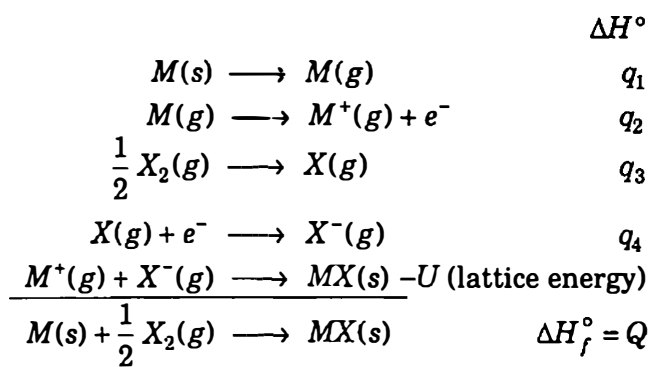
| Alkali metals 1  | Alkaline earths metals 2 |
|------------------|--------------------------|
| $1^1\text{H}$    |                          |
| $3^{\text{Li}}$  | $4^{\text{Be}}$          |
| $11^{\text{Na}}$ | $12^{\text{Mg}}$         |
| $19^{\text{K}}$  | $20^{\text{Ca}}$         |
| $37^{\text{Rb}}$ | $38^{\text{Sr}}$         |
| $55^{\text{Cs}}$ | $56^{\text{Ba}}$         |
| $87^{\text{Fr}}$ | $88^{\text{Ra}}$         |



- $\text{KO}_2$  has  $\text{O}_2^-$  ion (superoxide ion) and based on molecular orbital theory, bond-order is 1.5
- Amphoteric species are acidic (soluble in base) as well as basic (soluble in acid)
- Amphiprotic species is  $\text{H}^+$  ion donor as well as  $\text{H}^+$  ion acceptor



- Born-Haber cycle is based on Hess's law of constant heat summation and is used to derive Lattice energy of the compound and also other unknown parameter. For the salt  $\text{MX}(s)$



then  $q_1 + q_2 + q_3 + q_4 - U = Q$   
Thus,  $U$  is calculated.

## Introduction

Shells up to  $(n-1)$  are completely filled and differentiating (last) electron enters into  $ns$

Table 8.1 Periodicity in s-Block Elements

|          |                                                                                           |
|----------|-------------------------------------------------------------------------------------------|
| <i>A</i> | : Atomic number                                                                           |
| <i>B</i> | : Effective nuclear charge ( $Z^* = Z - \sigma$ )<br>where $\sigma$ is screening constant |
| <i>C</i> | : Number of shells                                                                        |
| <i>D</i> | : Atomic radius                                                                           |
| <i>E</i> | : Ionisation energy                                                                       |
| <i>F</i> | : Hydration and hydration energy                                                          |
| <i>G</i> | : Size of hydrated ion                                                                    |
| <i>H</i> | : Polarising power (based on Fajan's rule)                                                |
| <i>I</i> | : Lattice energy of chloride                                                              |
| <i>J</i> | : Reactivity                                                                              |
| <i>K</i> | : Ionic conductance                                                                       |

- From the Table 8.1, it is concluded that due to higher ( $IE$ ) of alkaline earth metals, they are less reactive than alkali metals.

sub-orbit—elements under this class are called **s-block elements**.

General electronic configuration of alkali group 1 (IA) is  $[\text{inert gas}] ns^1$  where  $n$  signifies group.

Alkali metals form compounds with +1 oxidation state in which stable nearest inert gas configuration is attained.

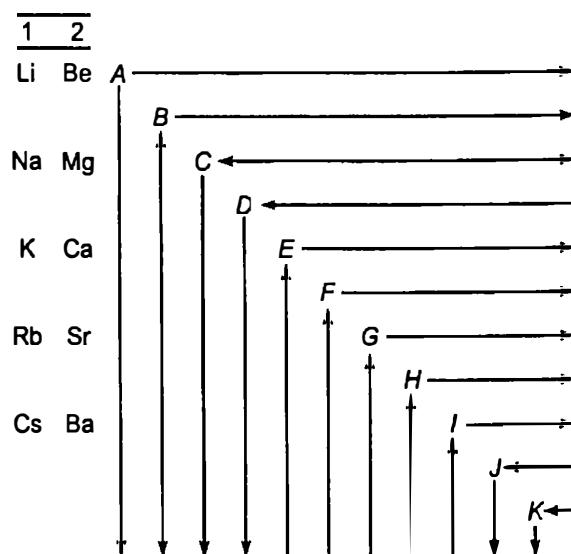
| Alkali metals |    |             |               | EC of $M^+$ (of IA) $M^{2+}$ (of IIA) |
|---------------|----|-------------|---------------|---------------------------------------|
| 1(IA)         | Z  | EC          | Ion           |                                       |
| Li            | 3  | [He] $2s^1$ | $\text{Li}^+$ | [He]                                  |
| Na            | 11 | [Ne] $3s^1$ | $\text{Na}^+$ | [Ne]                                  |
| K             | 19 | [Ar] $4s^1$ | $\text{K}^+$  | [Ar]                                  |
| Rb            | 37 | [Kr] $5s^1$ | $\text{Rb}^+$ | [Kr]                                  |
| Cs            | 55 | [Xe] $6s^1$ | $\text{Cs}^+$ | [Xe]                                  |
| Fr            | 87 | [Rn] $7s^1$ | $\text{Fr}^+$ | [Rn]                                  |

- Group IA elements are collectively known as alkali metals after the Arabic word *al-quis* meaning plant ashes which are rich in the carbonates of sodium and potassium.

## Periodicity at a Glance

Detailed periodicity has been given in chapter 3. Table 8.1 describes periodicity of s-block elements at a glance.

- There is uniform gradation in properties except in case of Li and Be which being smallest in their groups show abnormal behaviour. Li resembles Mg and Be resembles Al that we call **diagonal relationship**.



## Role of s-Block Ions in Biological Systems

- The sodium and potassium ions, taken together, constitute **sodium pump** which is also known as ' $\text{Na}^+ - \text{K}^+$  pump'. Operation of this process is biological in each and every cell of all animals in which  $\text{Na}^+$  ions from intracellular fluids are transferred to

the extracellular fluids with the help of **carrier-proteins**'. Transfer of  $K^+$  ions is however, in a reverse way and thus an electrical potential gradient is set-up across the cell-membrane which is responsible for the nerve signals in animals.

- Some NaCl is essential in the diet of humans and other animals because many biological functions are controlled by the concentration of  $Na^+$  and  $Cl^-$  ions. The fact that salt has long been recognised as important is evident in surprising ways. For example, we are paid a "**salary**" for workdone. This word is derived from the Latin *salarium* which meant "salt-money" because Roman soliders were paid in salt.

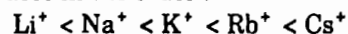
## Study of Group 1 (IA)—The Alkali Metals

The elements of group 1 (IA) illustrate, more clearly than any other group of elements, the effects of increasing the size of the atoms or ions on the physical and chemical properties which are closely related to their electronic structures (Table 8.2) and sizes.

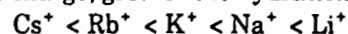
- The elements are all metals, excellent conductors of electricity, and are typically soft and highly reactive.
- They have one loosely held valence electron ( $ns^1$ ) in their outer shell, and thus form univalent, ionic and colourless compounds.  $M^+$  has stable nearest noble gas configuration.
- The hydroxides and oxides are very strong bases and the oxo salts are very stable.
- Lithium, the first element in the group, shows considerable difference from the rest of the group. This is due to high charge density of the  $Li^+$  ion compound compared to other alkali metal ions. (charge density = ionic charge/ionic radius)

### DEEP Focus

- Ionic size increases in the order :



and size of hydrated ion increases in the order (smaller the size, larger the charge, greater the hydration) :



hence ionic conductance is in order :

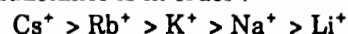


Table 8.2 Electronic Structure

| Element   | Symbol | Z  | Electronic structure                                                            |
|-----------|--------|----|---------------------------------------------------------------------------------|
| Lithium   | Li     | 3  | $1s^2 2s^1$ [He] $3s^1$                                                         |
| Sodium    | Na     | 11 | $1s^2 2s^2 2p^6 3s^1$ [Ne] $3s^1$                                               |
| Potassium | K      | 19 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ [Ar] $4s^1$                                     |
| Rubidium  | Rb     | 37 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^6 5s^1$ [Kr] $5s^1$                           |
| Caesium   | Cs     | 55 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ [Xe] $6s^1$ |
| Francium  | Fr     | 87 | $... .. 6s^2 6p^6 7s^1$ [Rn] $7s^1$                                             |

- All the alkali metals give characteristic colours in bunsen flame. On heating in bunsen flame, outermost electrons get excited to higher energy levels (due to very low  $(IE)_1$ . When these electrons return to the ground state absorbed energy is released in the form of light in the visible region of the spectrum.

| Element | Colour        | $\lambda/nm$ |
|---------|---------------|--------------|
| Li      | crimson red   | 670.8        |
| Na      | golden yellow | 589.2        |
| K       | violet        | 766.8        |
| Rb      | red violet    | 780.0        |
| Cs      | blue          | 455.5        |

Colour emission by these elements is the basis of analytical methods (like flame photometry, atomic absorption spectroscopy) for the precise estimation of these metals.

### Occurrence and Uses of Alkali Metals

| Element   | Abundance                                                                                                   | Main mineral                                                                                                                                          | Uses                                                                              |
|-----------|-------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|
| Lithium   | 0.002%                                                                                                      | First isolated in 1817 from petalite ( $LiAlSi_4O_{10}$ ) named after the Greek word lithos meaning stone. Main source is spodumene ( $LiAlSi_2O_6$ ) | All-purpose automotive grease.                                                    |
| Sodium    | 2.36% sixth most abundant element in the earth's crust and the most abundant metal, after Al, Fe, Ca and Mg | First prepared in 1807 from caustic soda, NaOH. NaCl (halite or rock salt), $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ (trona) (saltpeter) are main sources | Glass, rubber, pharmaceutical agents use sodium or its salts in their production. |
| Potassium | 2.09% eighth most abundant element in the earth's crust and next most abundant metal after Na.              | First prepared in 1807, name derived from potash ( $K_2CO_3$ ) KCl (sylvite), $KCl \cdot MgCl_2 \cdot 6H_2O$ (carnallite) are main sources.           | As a plant fertilizer.                                                            |

Although Na and K are almost equally abundant in the crusted rocks of the earth, Na is some 30 times as

abundant as K in the oceans. This is partly because K salts with the larger anions tends to be less soluble than the Na

salts and like wise, K is more strongly bound to the complex silicates and aluminosilicates in soils (ion exchange in clays)

Also K leached from rocks is preferentially absorbed and used by plants whereas Na can proceed to sea.

The Alkalide Ions

The reaction  $2\text{Na}(g) \rightleftharpoons \text{Na}^+(g) + \text{Na}^-(g)$  is endothermic by  $438 \text{ kJ mol}^{-1}$  which indicates  $-1$  oxidation state nonexistent but under unusual conditions this  $-1$  state exists as in crown ethers (polycyclic ethers).

Solutions of sodium in ethylenediamine or methylamine show electrical conductance of normal 1 : 1 electrolytes— possibly due to  $\text{Na}^+$  and  $\text{Na}^-$ . Alkali metals also dissolve in certain ethers, tetrahydro furan and other solvents forming relatively unstable solutions. The optical spectra of such solutions clearly indicate two distinct

absorption bands — one for the solvated electrons and the other for the  $M^-$  species called alkalide ion. This is supported by the following facts :

- (i) The solutions are diamagnetic, as expected for spin-paired  $M^-$  ions in the ground state.
- (ii) The molar conductivity of solutions containing sodium decreases slowly as the concentration is raised. This is due to the formation of ion pairs  $\text{Na}^+ \text{Na}^-$ .
- (iii) Absorption band also confirms the existence of  $\text{Na}^-$

Periodicity of Alkali Metals

Table 8.3 summarises physical properties of the elements of group 1 (IA). From this we conclude

- they have low  $(IE)_1$
- they have large negative electrode potentials
- they are a group of active metals.

Table 8.3 Properties of the Alkali Metals

| Properties                                                                                                                 | Li     | Na     | K      | Rb     | Cs     |
|----------------------------------------------------------------------------------------------------------------------------|--------|--------|--------|--------|--------|
| Effective nuclear charge                                                                                                   | 1.3    | 2.2    | 2.2    | 2.2    | 2.2    |
| Metallic radius (pm)                                                                                                       | 123    | 157    | 203    | 216    | 235    |
| Ionic radius (pm)                                                                                                          | 76     | 102    | 138    | 152    | 167    |
| Ionic charge density<br>(ionic charge/ionic radius (Å))                                                                    | 1.32   | 40.98  | 0.72   | 0.66   | 0.60   |
| Radius of hydrated ions (pm)                                                                                               | 340    | 276    | 232    | 228    | 220    |
| (EN), electronegativity                                                                                                    | 1.0    | 0.9    | 0.8    | 0.8    | 0.7    |
| Melting point (°C)                                                                                                         | 181    | 98     | 63     | 39     | 29     |
| Boiling point (°C)                                                                                                         | 1331   | 890    | 766    | 701    | 688    |
| Density ( $10^3 \times \text{kg m}^{-3}$ )                                                                                 | 0.53   | 0.97   | 0.86   | 1.53   | 1.87   |
| $(IE)_1, M(g) \rightarrow M^+(g) + e^-$<br>or $\Delta H^\circ_{\text{ionis.}}$ ( $\text{kJ mol}^{-1}$ )                    | 520    | 496    | 419    | 403    | 376    |
| $(IE)_2, M^+(g) \rightarrow M^{2+}(g) + e^- \text{ kJ mol}^{-1}$                                                           | 7297   | 4561   | 3069   | 2650   | 2420   |
| Sublimation energy<br>$M(s) \rightarrow M(g), \Delta H^\circ_{\text{subl.}}$ ( $\text{kJ mol}^{-1}$ )                      | 155    | 109    | 90     | 86     | 79     |
| Hydration energy<br>$M^+(g) \longrightarrow M^+(aq), \Delta H^\circ_{\text{hydr.}}$ ( $\text{kJ mol}^{-1}$ )               | -506   | -397   | -318   | -289   | -259   |
| $\Delta H^\circ_{\text{subli.}} + \Delta H^\circ_{\text{ionis.}} + \Delta H^\circ_{\text{hydr.}}$ ( $\text{kJ mol}^{-1}$ ) | 169    | 208    | 191    | 200    | 196    |
| $E^\circ_{\text{red}}(V), M^+(aq) + e^- \longrightarrow M(s)$                                                              | -3.045 | -2.714 | -2.925 | -2.925 | -2.923 |
| Abundance on Earth%                                                                                                        | 0.002  | 2.36   | 2.09   | 0.009  | 0.0001 |
| Ionic mobility                                                                                                             | 33.5   | 43.5   | 64.5   | 67.5   | 68.0   |
| Lattice energy (of MCl), $\Delta H^\circ_{\text{U}}$ $\text{kJ mol}^{-1}$                                                  | -845   | -770   | -703   | -674   | -644   |
| $\Delta S^\circ_{\text{hydr.}}$ of $M^+$ , $\text{JK}^{-1} \text{ mol}^{-1}$                                               | -140   | -110   | -70    | -70    | -60    |
| $\Delta G^\circ_{\text{hydr.}}$ of $M^+$ , $\text{kJ mol}^{-1}$                                                            | -485   | -379   | -308   | -285   | -362   |

1. Size

Alkali metals are the largest in their corresponding periods in the Periodic Table. The size of the atom or its ion increases on descending the group. This is due to the addition of an extra shell of electrons as we move down the

group from one element to the next. The addition of the extra shell of electrons overweighs the effect of increased nuclear charge and thus there is an increase in size from Li to Cs. The size is based on

$$r_n = \frac{n^2 a_0}{Z^*}$$

where  $n$  = number of shells

$a_0$  = Bohr's radius

$Z^*$  = Effective nuclear charge due to screening

( $Z^* = 1.3$  for Li and  $2.2$  for Na—Fr)

Thus, atomic ionic size is mainly dependent on  $n$ .

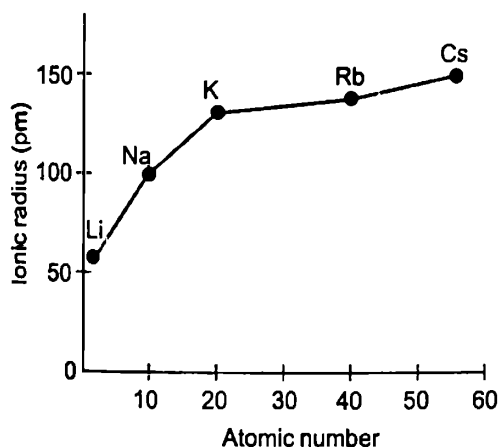


Fig. 8.1 Trend in ionic radii of group one elements.

## 2. Density

In a group, density increases on going down the group. Since, the elemental structure are often the same within any group, the factors which determine the density are atomic mass and volume. In this group, increase in atomic weight from one element to the next in passing down the group outweighs the effect of increase in the size of the atom. Density of potassium is however less than that of sodium.

## 3. Melting Point and Boiling Point

These metals are soft and can be cut with a knife. As a result of increase in size and repulsion of the non-bonded electrons, their cohesive energy and tendency for metallic bonding decrease down the group and thus softness increases from Li to Cs. These metals have low melting point and boiling point which also reflect the low values of cohesive energy between the atoms.

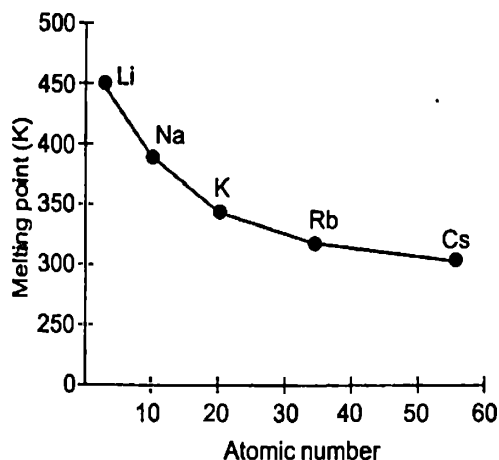


Fig. 8.2 Trend in the melting point of group one elements.

## 4. Thermal and Electrical Conductivity

In alkali metals, electrons of the noble gas core efficiently shield the lone valence shell electron from the nuclear charge. Thus, effective nuclear charge felt by the electron in the valence shell of an atom of an alkali metal is the least and the sole valence shell electron is very loosely held by the nucleus. It can move freely from one metal to the other in the lattice, thereby the alkali metals are good conductors of heat and electricity. **The loosely bound electron is also responsible for the silvery lustre of the alkali metals when freshly cut.**

## 5. Ionisation Energy, Electrode Potential and Hydration Energy

Low values of  $(IE)_1$  reflect the tendency of the element to oxidise — the electropositive character. Rb and Cs are so highly electropositive that they emit electrons even when exposed to light, that is they exhibit photoelectric effect.

- What is the significance of the large negative electrode potentials of the alkali metals? They mean that the metal  $M^+$  can be reduced to the free metal  $M$  only with great difficulty. On the other hand, the reverse process— oxidation of the metals occurs with great ease.

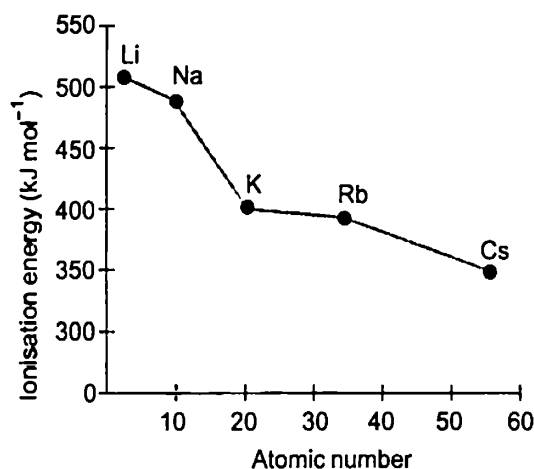


Fig. 8.3 Trend in first ionisation of alkali metals.

### DEEP Focus

- If we use the magnitude of the first ionisation energy  $(IE)_1$  as an indicator of ease of oxidation, Li is the most difficult of the alkali metals to oxidise. On the other hand, if we use  $E^\circ_{\text{redn.}}$  (standard reduction electrode potential) as our criterion, Li is the easiest to oxidise. How can we explain this discrepancy? Actually these two criteria  $(IE)_1$  and  $E^\circ_{\text{redn.}}$  measure the same thing.  $(IE)_1$  measures the tendency for a gaseous atom to ionise,  $E^\circ_{\text{redn.}}$  measures the tendency for a metal atom to go from solid state to the ion in aqueous solution which involves:

- (1) subliming the solid metal to the gaseous state
- (2) ionising the gaseous metal atoms to gaseous metal ions
- (3) hydrating the ions by dissolving  $M^+(g)$  in water to produce  $M^+(aq)$

$$\begin{aligned}\text{Thus, } \Delta H_{\text{ox}}^\circ &= \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ \\ &= \Delta H_{\text{subli.}}^\circ + \Delta H_{\text{ionis.}}^\circ + \Delta H_{\text{hydr.}}^\circ\end{aligned}$$

From Table 8.3, it is clear that they ( $\Delta H_{\text{oxdn.}}^\circ$ ) are positive values, but that the value is smallest for Li (169 kJ). This is primarily because of the large negative  $\Delta H$  for the hydration of  $\text{Li}^+$ . Thus it appears that **Li(s) should be easiest to oxidise of the alkali metals**. If lithium takes part in reactions that do not involve water, then it does show less reducing power than the other members of the group.

In terms of lattice energy  $\Delta H_U^\circ$ , heat of solution is

$$\Delta H_{\text{solution}}^\circ = \Delta H_{\text{hydra.}}^\circ - \Delta H_U^\circ$$

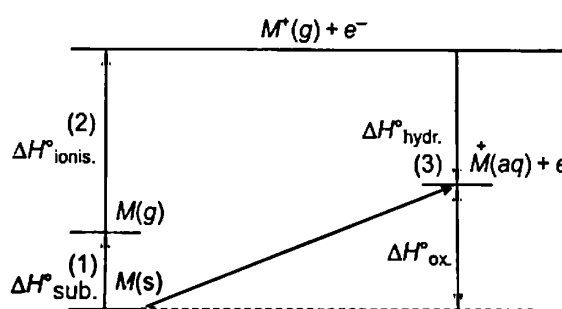
In general, if  $\Delta H_{\text{hydra}}^\circ > \Delta H_U^\circ$ , or  $\Delta H_{\text{solution}}^\circ > 0$ , the salt dissolves in water.

For NaCl  $\Delta H_{\text{hydra}}^\circ = -772 \text{ kJ mol}^{-1}$

$$\Delta H_U^\circ = -776 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{solution}}^\circ = -772 - (-776) = 4 \text{ kJ mol}^{-1}$$

hence NaCl dissolves in water.



- With increase in atomic number, the atoms become larger and the strength of the metallic bonding decreases.
- Enthalpies of hydration ( $\Delta H_{\text{hydr}}^\circ$ ) and entropies of hydration ( $\Delta S_{\text{hydr}}^\circ$ ) both become less negative as ionic size increases, but the variation in free energy of hydration ( $\Delta G_{\text{hydr}}^\circ$ ) follows fairly closely that in enthalpy of hydration.
- Due to the fact that the due to the largest size of the hydrated  $\text{Li}^+$  ion, it is least conducting in solution order being  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ .

## Gradation in the Properties of Alkali Metals

|                     |    |                     |     |
|---------------------|----|---------------------|-----|
| Atomic radii        | Li | m.p. and b.p.       | max |
| Atomic volume       | Na | Hardness            |     |
| Density             | K  | Ionisation energy   |     |
| Reactivity          | Rb | Conductivity        |     |
| Reducing power      | Cs | Electronegativity   |     |
| Electropositivity   |    | Solubility of salts |     |
| Anion stabilisation |    | having large anions |     |
| Solubility of salts |    |                     |     |
| having small anions |    |                     | max |

## DEEP Focus

- Standard electrode potentials ( $E_{M^+/M}^\circ$ ) are related to energy changes of the process of atomisation (sublimation), ionisation and hydration; among the alkali metals these changes almost cancel one another and  $E_{M^+/M}^\circ$  for the different  $M^+/M$  systems is nearly constant. The lower reactivity of Li towards water is therefore kinetic rather than thermodynamic in origin: as a harder and less easily melted metal, Li is less easily dispersed and hence, reacts more slowly than the other metals.
- The second ionisation energies,  $(IE)_2$ , of all alkali metals are so high that the formation of  $M^{2+}$  ions under chemically realisable conditions is not possible.
- All of the halides ( $\text{MX}$ ,  $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) have strongly negative standard enthalpy of formation,  $\Delta H_f^\circ$ , but the actual values show two different trends as is evident from Table 8.4.
  - (a)  $\Delta H_f^\circ$  for fluorides becomes less negative as we go down the group, while reverse is true for chlorides, bromides and iodides.
  - (b) For a given metal,  $\Delta H_f^\circ$  always becomes less negative as we go from the fluoride to iodide.

Table 8.4 Standard Enthalpies of Formation of Alkali Metal Halides

| M  | $\Delta H_f^\circ (\text{MX})/\text{kJ mol}^{-1}$ |      |      |      |
|----|---------------------------------------------------|------|------|------|
|    | MF                                                | MCl  | MBr  | MI   |
| Li | -617                                              | -409 | -351 | -270 |
| Na | -575                                              | -411 | -361 | -288 |
| K  | -568                                              | -436 | -394 | -328 |
| Rb | -557                                              | -443 | -393 | -333 |
| Cs | -555                                              | -435 | -405 | -348 |

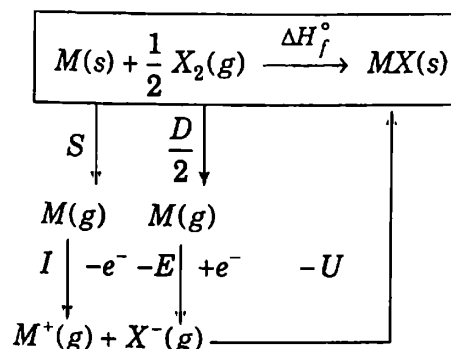
## 6. Lattice Energy and Solubility

As shown in Table 8.5, the variation in lattice energy (which is defined as the energy released when cations and anions in gaseous state combine to form one mole of ionic crystals) for fluorides is greater than the variation in lattice energy for chlorides, bromides and iodides. This is

because lattice energy is proportional to  $\left(\frac{1}{r_+ + r_-}\right)$  and to

the charge on the ions hence, the variation in lattice energy is the greatest when  $r_-$  is smallest and least when  $r_-$  is largest. **Lattice energy is the driving force for the formation of an ionic compound and its stability.**

Lattice energy is measured by **Born-Haber cycle**



$S$  = heat of sublimation of  $M(s)$

$I$  = ionisation energy of  $M(g)$

$D$  = dissociation energy of  $X_2(g)$

$E$  = electron-affinity of  $X(g)$

$U$  = lattice energy of  $MX(s)$

$\Delta H_f^\circ$  = heat of formation of  $MX(s)$

Based on above cycle

$$\Delta H_f^\circ = S + I + \frac{D}{2} - E - U$$

$$\therefore U = -\Delta H_f^\circ + S + I + \frac{D}{2} - E$$

The solubility of most of the salts of group 1 (alkali metals) elements  $M$  water **decreases on descending the group**. For a substance to dissolve, the energy evolved when the ions are hydrated (hydration energy) must be larger than the energy required to break the crystal lattice (crystal energy). We can say that if the solid is insoluble.

**Hydration Energy < Lattice energy**

In case of alkali metals, lattice energy only changes slightly, but the free energy of hydration changes rather more.

|                                    | Free energy of hydration<br>$\Delta G_{\text{hydration}}^{\circ}$ | Lattice energy<br>$MCl$ (U) |                  |
|------------------------------------|-------------------------------------------------------------------|-----------------------------|------------------|
| $\text{Li}^{+}$                    | -485                                                              | -845                        | difference<br>67 |
| $\text{Na}^{+}$                    | -379                                                              | -770                        |                  |
| $\text{K}^{+}$                     | -308                                                              | -703                        |                  |
| $\text{Rb}^{+}$                    | -285                                                              | -674                        |                  |
| $\text{Cs}^{+}$                    | -362                                                              | -644                        |                  |
| all values in $\text{kJ mol}^{-1}$ |                                                                   |                             |                  |

Difference in lattice energy between  $NaCl$  and  $KCl$  is  $67 \text{ kJ mol}^{-1}$ , and yet the difference in  $\Delta G_{\text{(hydration)}}$  for  $Na^+$  and  $K^+$  is  $71 \text{ kJ mol}^{-1}$ . Thus,  $KCl$  is less soluble than  $NaCl$ .

Table 8.5 Lattice Energies of Alkali Metal Halides

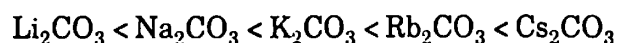
| $M$ | $U (MX)/\text{kJ mol}^{-1}$ |       |       |      |
|-----|-----------------------------|-------|-------|------|
|     | $MF$                        | $MCl$ | $MBr$ | $MI$ |
| Li  | -1035                       | -845  | -800  | -740 |
| Na  | -908                        | -770  | -736  | -690 |
| K   | -803                        | -703  | -674  | -636 |
| Rb  | -770                        | -674  | -653  | -615 |
| Cs  | -720                        | -644  | -623  | -590 |

We observe that the lattice energies decrease regularly from  $Li$  to  $Cs$  and from  $F^-$  to  $I^-$ . (Table 8.5).

- The higher the charge and the smaller the size of the ion, the more is the hydration energy. In a group, lattice energy and hydration energy decrease as we go down. While the decrease in lattice energy favours the solubility, the decrease in hydration energy makes the compound insoluble.

### DEEP Focus

- Another important factor contributing to the solubility of the compound is the comparison of the size of cation and anion. Whenever cation is small and anion is large or *vice-versa*, the solubility will be larger. Thus, solubility of  $CsF > CsCl > CsBr > CsI$  and solubility of  $LiF < LiCl < LiBr < LiI$ .
- $LiCl$ ,  $LiBr$ ,  $LiI$ , and  $NaI$  are readily soluble in some oxygen-containing organic solvents such as ether.  $NaI$  and  $LiI$  both are very soluble and form complexes in  $NH_3$ . The unstable complex  $[Na(NH_3)_4]I$  has been isolated and shown to contain a tetrahedrally coordinated sodium ion.
- In the vapour phase, alkali metal halides are present as ion-pairs, but measurement of bond length and dipole moment suggests that under these conditions electron-sharing is also involved to a considerable extent, especially for the lithium halides.
- For the salts of small anions (like  $F^-$ ,  $OH^-$ ,  $O^{2-}$ ,  $CO_3^{2-}$  etc.), lattice energy which is inversely proportional to  $(r_+ + r_-)$  is very sensitive to the change in the size of the cation, and anion being very small in size has little contribution in the total and decreases sharply along the group, and decrease in lattice energy is greater than decrease in hydration energy and thus solubility of these salts increases as we go down the group. Solubility of the alkali fluorides is thus in order:



### Thermal Stability of Salts

The stability of the compounds can also be explained by using the concept of polarising power. The simple idea

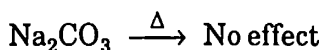
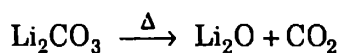
is that, as the charge density of the metal ions increases, the thermal stability of the salts of large polarisable anions, relative to some decomposition product decreases. In general, the least polarising metal ions are those of the most electropositive metal ions and these from the most stable salts with large anions. In other words, **small cations form stable salts with small anions and large cations form stable salts with large**

### DEEP Focus

Small cations and small anions  
or  
Large cations and large anions

Stable salts

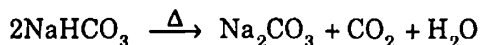
**anions.** Let us take the example of carbonates of Group I metals. The carbonates of sodium, potassium rubidium and caesium are resistant to the heat of a bunsen burner flame, however, lithium carbonate decomposes to its oxide and carbon dioxide under the same conditions :



The tendency of  $\text{Li}_2\text{CO}_3$  to undergo thermal decomposition may be explained in terms of the gain in electrostatic attraction that occurs when **extremely small  $\text{Li}^+$**  ion combines with the smaller oxide ion rather than the much **larger carbonate ion**. The other carbonates of Group I (Na–Cs) are more stable because the cations have a lower charge density and considerably larger in size and thus decomposition is less favourable energetically.

### DEEP Focus

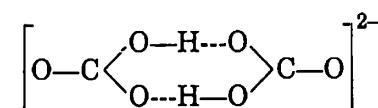
All the metals except lithium form stable bicarbonates (lithium bicarbonate is formed only aqueous solutions and has not been isolated. It is due to strong polarising power of  $\text{Li}^+$  on the  $\text{HCO}_3^-$  ion of larger size.) When we heat the alkali metal bicarbonates, they are decomposed to carbonates and simultaneously, carbon dioxide and water are liberated.



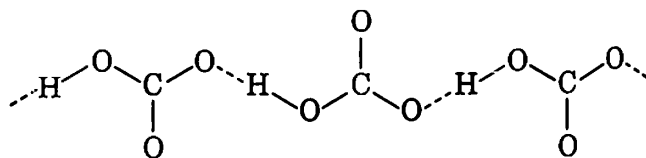
This reaction forms the basis for the use of  $\text{NaHCO}_3$  in baking powder.

As the electropositive character increases down the group the stability of carbonates and bicarbonates increases. ( $\text{Na} < \text{K} < \text{Rb} < \text{Cs}$ )

The crystal structures of  $\text{NaHCO}_3$  and  $\text{KHCO}_3$  both show hydrogen bonding, but are different. In  $\text{NaHCO}_3$  the  $\text{HCO}_3^-$  ions are linked into **infinite chain**, while in  $\text{KHCO}_3$  a dimeric anion is formed.

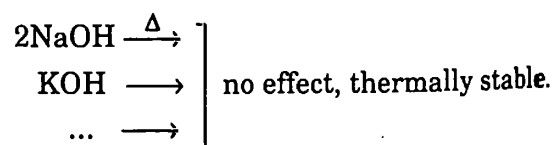
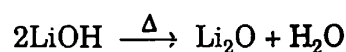


H-bonding in  $\text{KHCO}_3$  (a-dimer)



H-bonding in  $\text{NaHCO}_3$  (a-chain)

The thermal stability of Group I hydroxides also follows a similar trend as that of carbonates. Thus, except  $\text{LiOH}$ , which on heating decomposes to  $\text{Li}_2\text{O}$ , all other Group I hydroxides are stable.



The ease of thermal decomposition of a salt is related to the **enthalpy of formation** of the salt. The **enthalpy of formation**,  $\Delta H_f^\circ$ , of a salt  $MA$  ( $M$  is the metal,  $A$  is anion) is given by

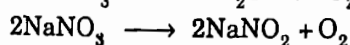
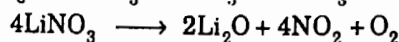
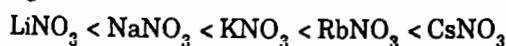
$$\Delta H_f^\circ = (\Delta H_{\text{atom}} + I)_{\text{metal}} + (\Delta H_{\text{atom}} - E_A)_{\text{anion}} - \Delta H_{\text{lat}}$$

where  $\Delta H_{\text{atom}}$  is the **enthalpy of atomisation**,  $I$  is the ionisation energy and  $E_A$  is the electron affinity. Since for any salt in a particular group the terms involving the anion alone remain constant, the value of  $\Delta H_f^\circ$  for such compounds is dependent upon the sum of the enthalpy terms of the particular metal,  $(\Delta H_{\text{atom}} + I)_{\text{metal}}$  and the lattice energy,  $\Delta H_{\text{lat}}$ . The larger the lattice energy, the more negative the enthalpy of formation and so, more stable is the compound. All these terms become smaller on descending the series from lithium to caesium. The relative stabilities of the salts are, therefore, decided by the parameter which decreases more rapidly—the lattice energy or the sum of the metal enthalpies.

In the salts having **small anions of high charge density**, e.g.,  $\text{F}^-$ ,  $\text{N}^{3-}$ ,  $\text{OH}^-$ ,  $\text{O}^{2-}$  etc., the **change in lattice energy is much dependent on the size of the cation and decreases rapidly on descending the group**. Thus, as the size of the cation increases, lattice energy decreases more than the change in the sum of the metal enthalpies. Therefore, as we go down the group, the stability of these salts having small anions decreases. Thus, in alkali metal fluorides, the stability decreases in the order  $\text{LiF} > \text{NaF} > \text{KF} > \text{RbF} > \text{CsF}$ .

**DEEP Focus**

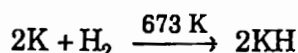
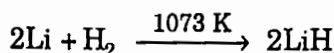
Similarly, lithium nitrate also decomposes on heating to give  $\text{Li}_2\text{O}$ ,  $\text{NO}_2$  and  $\text{O}_2$  but all other alkali metal nitrates decompose on strong heating to nitrites liberating oxygen: Stability being



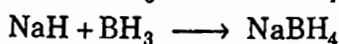
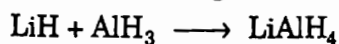
- The increasing stability of the peroxides ( $\text{M}_2\text{O}_2$ ) or superoxides ( $\text{MO}_2$ ), as the size of the metal ion increases is due to the stabilisation of large anions by larger cations through lattice energy effects.
- The m.p. and b.p. of alkali halides always follow trend  $\text{MF} > \text{MCl} > \text{MBr} > \text{MI}$ .

**Hydride**

The alkali metals react with  $\text{H}_2$  at high temperature to form the hydrides.



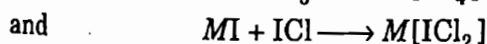
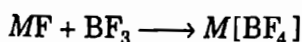
- Metallic hydrides are ionic solids with high melting points. They form complex hydrides when find applications in synthesis of organic compounds.



They also react with proton donors such as alcohols, gaseous ammonia and alkynes.

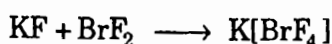
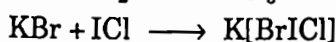
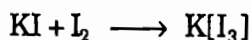
**Complex Halide and Polyhalides**

Complex halide formation such as represented by the equations :

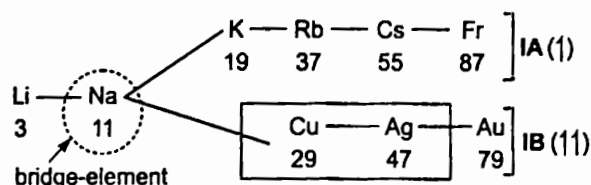


is favoured by increase in the size of the cation.

- The alkali metal halides react with the halogen and interhalogen compounds forming ionic polyhalide compounds

**Alkali and Coinage Metals**

Elements of group I except hydrogen are all metals arranged in two sub-groups:



(1) IA — Li, Na, K, Rb, Cs, Fr

(11) IB — Cu, Ag, Au.

Sodium (11) acts as a bridge for sub-groups A and B. Distinction between alkali and coinage metals has been summarised below:

| Properties                  | IA(1)                                                                                                                                                                             | IB(11)                                                                                                                                                                                                                              |
|-----------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1. Electronic configuration | [Inert gas] $ns^1$                                                                                                                                                                | [Inert gas] $(n-1)d^{10}ns^1$                                                                                                                                                                                                       |
| 2. Block                    | s-block                                                                                                                                                                           | d-block                                                                                                                                                                                                                             |
| 3. (IE)                     | low, form stable $M^+$ ion                                                                                                                                                        | higher than IA, form $M^+$ ion, Cu also forms $\text{Cu}^{2+}$ while Au form $\text{Au}^{3+}$ salts                                                                                                                                 |
| 4. Reactivity               | highly reactive with water                                                                                                                                                        | even non-reactive with water but tarnished by air                                                                                                                                                                                   |
| 5. Nature of salts          | halides, nitrates, bicarbonates soluble (Li <sup>+</sup> exception, its salts are predominantly covalent due to smaller size)                                                     | sulphates, carbonates, water CuS, Ag <sub>2</sub> S etc., insoluble                                                                                                                                                                 |
| 6. Size of ions             | larger than coinage metal<br>$\text{Na}^+ > \text{Cu}^+, \text{K}^+ > \text{Ag}^+$                                                                                                | Smaller than alkali metal                                                                                                                                                                                                           |
| 7. Electropositive nature   | placed above H in electrochemical series, more reactive than coinage metals<br>$\text{Li}^+(\text{aq}) + e^- \longrightarrow \text{Li}(\text{s})$<br>$E^\circ = -3.045 \text{ V}$ | placed below H in electrochemical series, hence, less reactive than alkali metals, do not displace $\text{H}_2$ with acids<br>$\text{Cu}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Cu}(\text{s})$<br>$E^\circ = +0.34 \text{ V}$ |

**Reactions of Group I Metals**

Alkali metals, due to low (IE), are reactive and are always found in combined state. Table 8.6 summarises reactions of alkali metals. The reactivity of the alkali metals increases from Li to Cs except towards  $\text{N}_2$ . The slow reactivity of Li is due to kinetic factor.



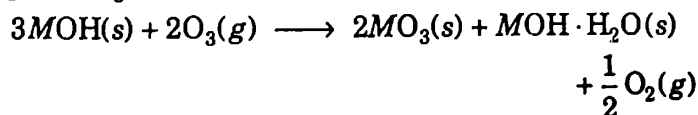
Table 8.6 Reactions of Group I Metals

| Reaction                                              | Comment                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |
|-------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $2M + 2H_2O \longrightarrow 2MOH + H_2$               | MOH are strongest bases. All alkali metals react with $H_2O$ . Lithium undergoes the reaction with vigorous bubbling as $H_2$ is released, sodium reacts rapidly with evolution of heat and potassium reacts so violently that $H_2$ produced bursts instantly into flame.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
| $2Li + \frac{1}{2}O_2 \longrightarrow Li_2O$          | Monoxide is formed by Li and to a small extent by Na (oxidation number (O.N.) of O = -2) Normal oxides $M_2O$ , ( $M = Li, Na, K, Rb$ ) have antifluorite structure. This structure is related to the $CaF_2$ structure but the sites occupied by the cations and anions interchanged so that $M$ replaces F and O replaces Ca in the structure.<br>There is a trend to increasing coloration with increasing atomic number,<br>$Li_2O, Na_2O$ — pure white<br>$K_2O$ — yellowish white<br>$Rb_2O$ — bright yellow<br>$Cs_2O$ — orange<br>Peroxide formed by Na and to a small extent by Li (O.N. of O = -1)<br>Superoxide ( $MO_2$ ) formed by K, Rb and Cs. Superoxides are coloured and paramagnetic (ON of O = -1/2)<br>Under appropriate conditions pure compounds $M_2O, M_2O_2$ and $MO_2$ can be prepared for all five metals. |
| $2Na + O_2 \longrightarrow Na_2O_2$                   |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| $K + O_2 \longrightarrow KO_2$                        |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| $2M + H_2 \xrightarrow{\Delta} 2MH$                   |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| $MH + H_2O \longrightarrow MOH + H_2$                 |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| $3Li + \frac{1}{2}N_2 \longrightarrow Li_3N$          | Only Li forms nitride, slow at room temperature rapid at elevated temperature.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
| $2Na + C_2H_2 \longrightarrow Na_2C_2 + H_2$          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| $2M + F_2 \longrightarrow 2MF$                        | All metals form fluorides, chlorides, bromides and iodides. The reactivity of the alkali metals increases as their ( $IE$ ) decreases giving reactivity order:<br>$Cs > Rb > K > Na > Li$<br>The higher members can form polyhalides, $KI_3$ ( $K^+$ and $I_3^-$ ) and $CsBr_3$ ( $Cs^+$ , $Br_3^-$ )<br>Very vigorous reaction. Polysulphides are also formed. They are zig-zag chain structure of sulphur atoms.                                                                                                                                                                                                                                                                                                                                                                                                                     |
| $2M + Cl_2 \longrightarrow 2MCl$                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| $2M + Br_2 \longrightarrow 2MBr$                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| $2M + I_2 \longrightarrow 2MI$                        |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| $2M + S \longrightarrow M_2S$                         |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| $2M + 2NH_3 \xrightarrow{Fe} 2MNH_2 + H_2$            | All the metals form amides. Dilute solutions of alkali metals in liquid $NH_3$ are dark blue in colour and the main species present are solvated electrons and the solvated metal ions. If the blue solution is allowed to stand, the colour slowly fades until it disappears owing to the formation of metal amide.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |
| $Na(l) \longrightarrow Na^+(l) + e^-$                 |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| $e^- + NH_3 \longrightarrow NH_2^- + \frac{1}{2} H_2$ |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| $Na^+(am) + e^-(am) + NH_3(l)$                        |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| $\longrightarrow NaNH_2(s) + \frac{1}{2} H_2$         |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |

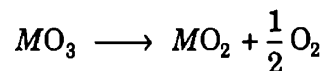
where 'am' denotes solution in ammonia.

Sesquioxide " $M_2O_3$ " have been prepared as dark-coloured paramagnetic powders by careful thermal decomposition of  $MO_2$  ( $M = K, Rb, Cs$ ) They can also be prepared by oxidation of liquid ammonia solutions of the metals or by controlled oxidation of the peroxides, and are considered to be peroxide disuperoxide [ $(M^+)_4(O_2^{2-})(O_2^-)_2$ ]

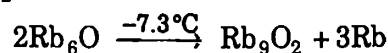
- Ozonides  $MO_3$  have been prepared for Na, K, Rb and Cs by the reaction of  $O_3$  on powdered anhydrous  $MOH$  at low temperature and extraction of the red  $MO_3$  by liquid  $NH_3$



The ozonides, on standing, slowly decompose to oxygen and the superoxide  $MO_2$ , but on hydrolysis forms  $MOH$



Rb and Cs also form suboxides in when the formal oxidation state of the metal is considerably lower. Partial oxidation of Rb at low temperature gives  $Rb_6O$  which decompose above  $-7.3^\circ C$  to give copper-coloured metallic crystals of  $Rb_9O_2$  :



Alkali metals react with  $H_2O$ , liberating  $H_2$  and forming hydroxides. The reaction becomes increasingly violent on descending the group. The Li reacts gently, sodium melts on the surface of water and molten metal even catches fire. Similarly for K.... Thus, Na, K are placed in **kerosene oil**.

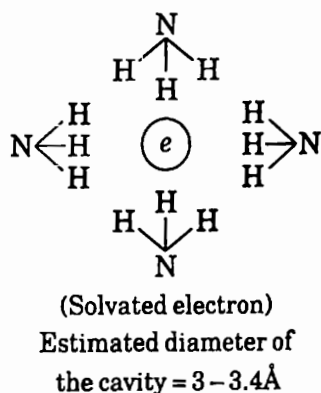
- Alkali metals are reactive and tarnish rapidly in dry air. Na, K, Rb and Cs form oxides of various types, but Li forms mixture of the oxide and the nitride,  $Li_2O$  and  $Li_3N$ . **Li is the only element of the alkali metals that forms nitride.**

## Solutions in Liquid Ammonia

The alkali metals dissolve in pure liquid ammonia without evolution of hydrogen; the metals can be recovered from such solution by evaporation. The saturation solubilities are quite high, e.g., at  $-33^\circ C$ .

| Element | Solubility in kg/kg $NH_3$ |
|---------|----------------------------|
| Li      | 108                        |
| Na      | 250                        |
| K       | 463                        |

**1. Colour** Dilute solution of alkali metals in liquid  $NH_3$  are blue due to solvated electrons and the solvated metal ions. But in the concentration of  $NH_3$  above 1M, metal ion cluster are formed, the solutions are copper-coloured with metallic lustre.

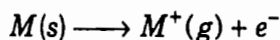


**2. Conductance and magnetic properties** The solutions are good conductors of electricity and are paramagnetic in nature, which decreases as concentration increases.

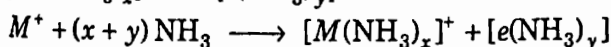
### Explanation

When alkali metal is dissolved in liquid  $NH_3$ , there is

**Step I.** Ionisation of alkali metal



**Step II.** Cation  $M^+$  and  $e^-$  both are solvated by  $NH_3$  forming  $[M(NH_3)_x]^+$  and  $[e(NH_3)_y]^-$ .

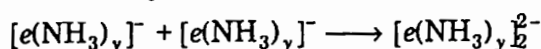


It is the **ammoniated electron** which is responsible for the blue colour of the solution, and the electrical conductivity is due to the ammoniated cation,  $[M(NH_3)_x]^+$  as well as the ammoniated electron,  $[e(NH_3)_y]^-$ , values of  $x$  and  $y$  depend on the extent of solvation (by  $NH_3$ ). Dilute solutions are paramagnetic due to free electrons. In concentrated solutions ammoniated electrons

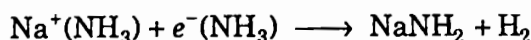
associate to form electron-pairs and their paramagnetic character decreases.

The solutions of alkali metals in liquid  $NH_3$  are extremely good conductors of electricity: they have higher conductivity than that of completely ionised salt in any known solvent. But the equivalence conductance decreases as the solution become more concentrated and reaches a minimum around 0.05 M. Beyond this concentration the conductivity increases dramatically sharply and the saturated solutions practically conduct electricity like liquid metals:

Conductivity of  $Hg \approx 10^4 \text{ ohm}^{-1}$  of Na in liquid  $\approx 0.5 \times 10^4 \text{ ohm}^{-1} NH_3$

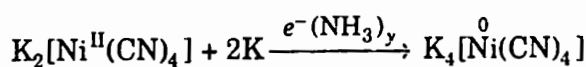
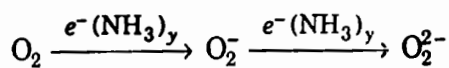


The solutions are themselves unstable with respect to amide formation.

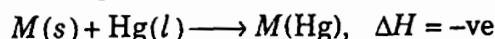


However, under anhydrous conditions and in the absence of catalytic impurities such as transition metal ions, solutions can be stored for several days.

**3. Reducing Property** Ammoniated solutions of alkali metals are reducing agents due to the presence of free or solvated electrons



- The alkali metals dissolve readily in mercury forming more reactive species  $M(Hg)$  called **amalgams**



Formation of an amalgam is an exothermic process.

## Solvation

When a metal ion is surrounded by the solvent molecules, the phenomenon is called **solvation** of the metal ion. When the solvent is water it is called **hydration**. The alkali metal ions are highly hydrated. The smaller the size of the ion, the greater is its degree of hydration. This is because the smaller the size, the more will be its charge density and the more will be its attraction for the polar solvent molecules. Thus,  $Li^+$  ion, which is the smallest gets more hydrated than the  $Na^+$  ion and so on. The degree of hydration decreases on moving down the group. As a result of differences in their degree of hydration, the hydrated ionic radii of the alkali metal ions decrease as we go down the group from lithium to cesium.  $Li^+$  ion has the largest hydrated radius while  $Cs^+$  has the smallest hydrated radius in the first group. One would agree that the smaller the size of the ion and the lighter it is, the more will be its mobility and thus conductance. In this regard we should expect the highest conductance for  $Li^+$  which is the smallest of the alkali metals but this is not

so. The hydrated radius of  $\text{Li}^+$  is the largest of all the alkali metal ions, in solution. Therefore,  $\text{Li}^+$  ion is the least conducting in solution. The ionic

conductance in solution actually decreases in the order  $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ .

## Target Practice 1

- Arrange Li, Na, K, Rb, Cs in increasing.
  - atomic radii
  - ionisation energy
  - electronegativity
  - electron-affinity
- Arrange alkali metal carbonates in increasing
  - thermal stability
  - covalent nature
  - melting point
  - lattice energy
- Compare hydration energy of
  - $\text{Na}^+$  and  $\text{Be}^{2+}$
  - $\text{Li}^+$  and  $\text{Be}^{2+}$
  - $\text{Li}^+$  and  $\text{Mg}^{2+}$
  - $\text{Be}^{2+}$  and  $\text{Al}^{3+}$
- The single-bonded metallic radius of sodium is 157 pm. Assume that the increment between radii of different magnitudes is 60 pm. Calculate the
  - covalent radius of Na
  - ionic radius  $\text{Na}^+$
  - ionic radius  $\text{Na}^-$
  - van der Waals' radius Na
- Write compounds of low solubility of Fr. ....
- How could you remove unreacted Na (metal) in liquid ammonia safely? .....

## Answers

- $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$
  - $\text{Cs} < \text{Rb} < \text{K} < \text{Na} < \text{Li}$
  - $\text{Cs} < \text{Rb} = \text{K} < \text{Na} < \text{Li}$
  - $\text{Cs} < \text{Rb} < \text{K} < \text{Na} < \text{Li}$
- $\text{Li}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{K}_2\text{CO}_3 < \text{Rb}_2\text{CO}_3 < \text{Cs}_2\text{CO}_3$
  - $\text{Cs}_2\text{CO}_3 < \text{Rb}_2\text{CO}_3 < \text{K}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{Li}_2\text{CO}_3$
  - $\text{Li}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{K}_2\text{CO}_3 < \text{Rb}_2\text{CO}_3 < \text{Cs}_2\text{CO}_3$
  - $\text{Cs}_2\text{CO}_3 < \text{Rb}_2\text{CO}_3 < \text{K}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{Li}_2\text{CO}_3$
- $\text{Be}^{2+} > \text{Na}^+$
  - $\text{Be}^{2+} > \text{Li}^+$
  - $\text{Mg}^{2+} > \text{Li}^+$
  - $\text{Al}^{3+} > \text{Be}^{2+}$
- 157 pm
  - 97 pm
  - 217 pm
  - 217 pm
- $\text{FrClO}_4, \text{Fr}_2\text{PtCl}_6$  (due to larger alkali metal ion)
- Add  $\text{NH}_4\text{Cl}$ , (a strong acid in  $\text{NH}_3$ )  

$$2\text{Na} + 2\text{NH}_4\text{Cl} \longrightarrow 2\text{NaCl} + \text{NH}_3 + \text{H}_2$$

## Practice Exercise 1

- Differentiating electron in K(19) goes into  $ns$  and this is  $s$ -block element. What happens if Aufbau rule is not followed?
- What would be electronic configuration of the following in the absence of Aufbau rule?
  - $\text{Ca}^{2+}$
  - $\text{Sr}^{2+}$
  - $\text{Rb}^+$
- Na and Mg are also called bridge element. Why?
- Which is more covalent in each pair?
  - LiCl or NaCl
  - LiCl or  $\text{BeCl}_2$
- $(IE)_1$  of the two elements of  $s$ -block of 2nd period are 520 and 899  $\text{kJ mol}^{-1}$ . Identify these elements.
- Compare Li and Be in the following properties:
  - $(IE)_1$
  - size of hydrated ion
  - polarisation (of cations)
  - thermal stability of carbonates
  - nature of oxide
  - nature of hydride
  - oxidation state
- Compare Li and Mg in the following properties:
  - effect of heat on their carbonates
  - hydration of chloride
  - nature of oxides
  - tendency to form nitrides
  - electronegativity
- Alkali metals are good reducing agents. Explain.
- $(IE)_1$  of Li is highest in first group but it is best reducing agent in aqueous solution. Explain.
- Arrange He, Li, Be, B, C, N, O, F, Ne in increasing second ionisation energy.
- In Table 9.3, size of the hydrated ion is in order  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ \geq \text{Cs}^+$  which is just reverse of ionic size. Explain.
- Calculate lattice energy of  $\text{NaCl}(s)$  from the following data:
 

heat of sublimation of  $\text{Na}(s) = S$   
 $(IE)_1$  of  $\text{Na}(g) = I$   
 bond dissociation energy of  $\text{Cl}_2(g) = D$   
 electron affinity of  $\text{Cl}(g) = -E$   
 heat of formation of  $\text{NaCl}(s) = -Q$
- Arrange the following in increasing lattice energy:
  - $\text{NaF}, \text{NaCl}, \text{NaBr}, \text{NaI}$
  - $\text{LiF}, \text{LiCl}, \text{LiBr}, \text{LiI}$
  - $\text{LiCl}, \text{NaCl}, \text{KCl}, \text{RbCl}, \text{CsCl}$
- A mixture contains 2 moles of  $\text{Na}_2\text{CO}_3$  and 1 mole of  $\text{Li}_2\text{CO}_3$ . Calculate volume of  $\text{CO}_2$  formed on heating this mixture and the data converted at STP.
- Identify (A), (B), (C), (D) and (E) in the following:
 

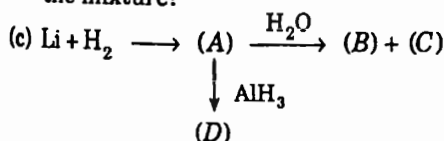
Alkali metal (A) +  $\text{N}_2 \xrightarrow{\Delta}$  (B)  $\xrightarrow{\text{H}_2\text{O}}$  (C) + (D)

(C) and (D) both react with HCl, but (D) gives white fumes (E) with HCl.

16. A binary salt (X) of alkali metal on heating with sulphur give (Y); (Y) with  $\text{BaCl}_2$  solution gave white ppt. (Z) insoluble in conc. HCl. 14.2 g of (X) gave 23.3 g of (Z). Identify (X), (Y) and (Z) and explain reactions.

17. (a) Which element of the alkali earth metals (group II) will form nitride?

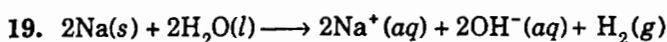
(b) 1 mole of a mixture of  $\text{Li}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  forms 0.75 mole of  $\text{CO}_2$  at NTP. What is percentage of each in the mixture?



What are (A), (B), (C) and (D)? What is main application of (D)?

18. Match the following column (A) with column (B):

| (A)                        | (B)                          |
|----------------------------|------------------------------|
| 1. $\text{KO}_2$           | (a) Diamagnetic              |
| 2. $\text{Na}_2\text{O}_2$ | (b) Conductor of electricity |
| 3. $\text{NaNH}_2$         | (c) Paramagnetic             |



Write the ON of all the atoms in various species.

## Answers

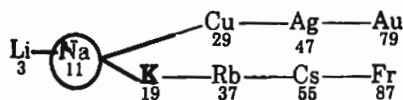
1. K(19) in the absence of Aufbau rule will have EC as:  $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1$  and thus differentiating electron enters into  $3d$ — a d-block element.

2. (a)  $\text{Ca}^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6$

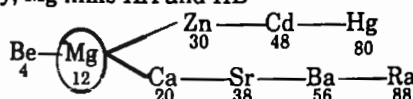
(b)  $\text{Sr}^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6$

(c)  $\text{Rb}^+ = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6$

3. Na is called bridge element since it links Group IA and Group IB



Similarly, Mg links IIA and IIB



4. (a)  $\text{LiCl}$  (b)  $\text{BeCl}_2$

Smaller cationic size, larger, charge, larger polarising power

5. Li and Be

6. (a)  $\text{Li} > \text{Be}$  (b)  $\text{Li}^+ < \text{Be}^{2+}$  (c)  $\text{Li}^+ < \text{Be}^{2+}$

(d)  $\text{Li}_2\text{CO}_3 > \text{BeCO}_3$  (e)  $\text{Li}_2\text{O}$ —basic (f)  $\text{LiH}$ —ionic

(g)  $\text{Li} = +1$   $\text{BeO}$ —amphoteric  $\text{BeH}_2$ —covalent  $\text{Be} = +2$

7. (a) Both decompose to form  $\text{CO}_2$  and oxide

(b) Both hydrated (c) Basic oxides

(d) Both form nitrides ( $\text{Li}_3\text{N}$ ,  $\text{Mg}_3\text{N}_2$ )

(e)  $\chi_{\text{Li}} = 1.0$   $\chi_{\text{Mg}} = 1.2$

8. In case of alkali metals, outer  $ns$ -electron is very well shielded by the inner electrons. Thus effective nuclear charge ( $= Z - \sigma$ ) is very small. As we go down the group, shielding wins over the effect of the increasing number of protons in the nucleus. Thus  $(IE)_1$  decreases, hence tendency to lose electrons, which is also a measure of the reducing nature, increases down the group.

9. See text

10.  $\text{Be} < \text{C} < \text{B} < \text{N} < \text{O} < \text{F} < \text{Ne} < \text{He} < \text{Li}$

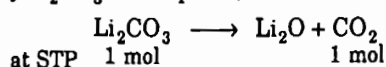
11. Greater the charge or charge density, smaller the ionic size, greater the hydration hence, greater the size of the hydrated ion.

12. Lattice energy  $-U = S + I + \frac{D}{2} - E - Q$

13. (i)  $\text{NaI} < \text{NaBr} < \text{NaCl} < \text{NaF}$  (ii)  $\text{LiI} < \text{LiBr} < \text{LiCl} < \text{LiF}$

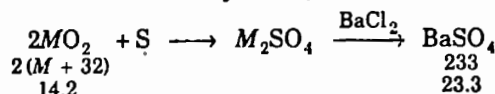
(iii)  $\text{CsCl} < \text{RbCl} < \text{KCl} < \text{NaCl} < \text{LiCl}$

14. 22.4 L (only  $\text{Li}_2\text{CO}_3$  decomposes)



15. (A) : Li (only Li forms nitride with  $\text{N}_2$ ) (B) :  $\text{Li}_3\text{N}$   
 (C) :  $\text{LiOH}$  (D) :  $\text{NH}_3$  (E) :  $\text{NH}_4\text{Cl}$

16. Let alkali metal be  $M$ , since  $X$  is binary and combines with  $S$  to give  $Y$ .  $Y$  gives white precipitate with  $\text{BaCl}_2$  insoluble in conc. HCl. It means  $Y$  has  $\text{SO}_4^{2-}$  and thus  $X$  is an oxide and thus,  $X$  is an oxide. Since  $X$  is binary hence,  $X$  is

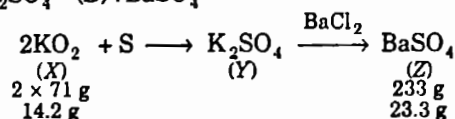


Thus,  $\frac{2(M + 32)}{14.2} = \frac{233}{23.3}$

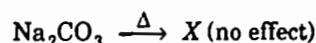
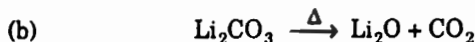
Thus,  $M = 39$ . Thus  $M$  is potassium.

(X) :  $\text{KO}_2$  (potassium superoxide,  $\text{K}^+\text{O}_2^-$  (binary))

(Y) :  $\text{K}_2\text{SO}_4$  (Z) :  $\text{BaSO}_4$



17. (a) Mg (due to diagonal relationship with Li)



$\text{CO}_2$  is due to  $\text{Li}_2\text{CO}_3$  only

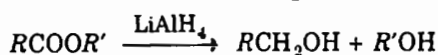
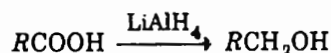
hence, 0.75 mol  $\text{CO}_2 = 0.75$  mol of  $\text{Li}_2\text{CO}_3$

75 mol %  $\text{Li}_2\text{CO}_3$

25 mol %  $\text{Na}_2\text{CO}_3$

(c) (A) :  $\text{LiH}$  (B) :  $\text{LiOH}$  (C) :  $\text{H}_2$  (D) :  $\text{LiAlH}_4$

(D) is a reducing agent in the preparation of alcohols from carbonyl compounds, acids, esters, etc.

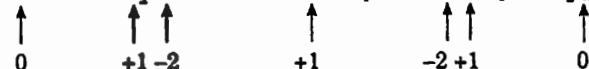
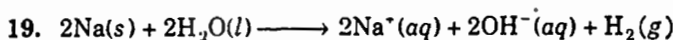


18. (A) (B)

1. c

2. a

3. b



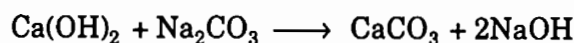
## Compounds of Sodium

- The metals of this group are too reactive to be found in the free state. Their compounds are amongst the most stable to heat, so thermal decomposition is impractical.
- The metals are the strongest chemical reducing agents and oxides can't be reduced to metals.
- The metals are generally obtained by electrolysis of a fused salt, usually the fused halide, often with impurity added to lower the melting point.
- Sodium is obtained by electrolysis of molten mixture of:
  - 40% NaCl
  - 60%  $\text{CaCl}_2$  in a Downs cell.

$\text{CaCl}_2$  lowers the m.p. of NaCl ( $803^\circ\text{C}$ ) to  $600^\circ\text{C}$ . Some Ca is formed but it remains insoluble in sodium, which collects at a copper or iron cathode that surrounds a circular graphite anode. Chlorine, a valuable by-product, collects at anode.

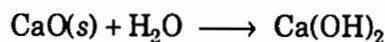
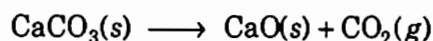
## Sodium Hydroxide

Until World War II, the **Soda-Lime process** the principal method of producing sodium hydroxide, NaOH, involved conversion of  $\text{Ca(OH)}_2$  to  $\text{CaCO}_3$  using  $\text{Na}_2\text{CO}_3$

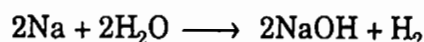


The reaction goes to completion as is evident by measuring pH of the solution after reaction.

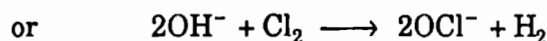
The insoluble  $\text{CaCO}_3$  by-product is filtered off, then heated (calcined) to convert it to lime ( $\text{CaO}$ ), which is recycled into the reaction system.



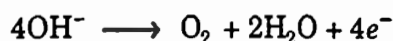
- Electrolysis of aqueous NaCl gives NaOH at cathode



Side reactions may also occur if the products formed mix with one each other.



and following reaction may also occur at the anode to a smaller extent:



## Nelson Cell (Diaphragm cell)

If  $\text{H}_2$  and  $\text{Cl}_2$  gases mix, they react with explosion. A porous diaphragm of asbestos is used to keep the  $\text{H}_2$  and  $\text{Cl}_2$  (and thus cathode and anode) gases separated from one another. Product in this cell is a mixture of 11% NaOH and 16% NaCl. Concentration in a steam evaporator gives solution containing 50% NaOH and 1% NaCl. (Fig. 8.4)

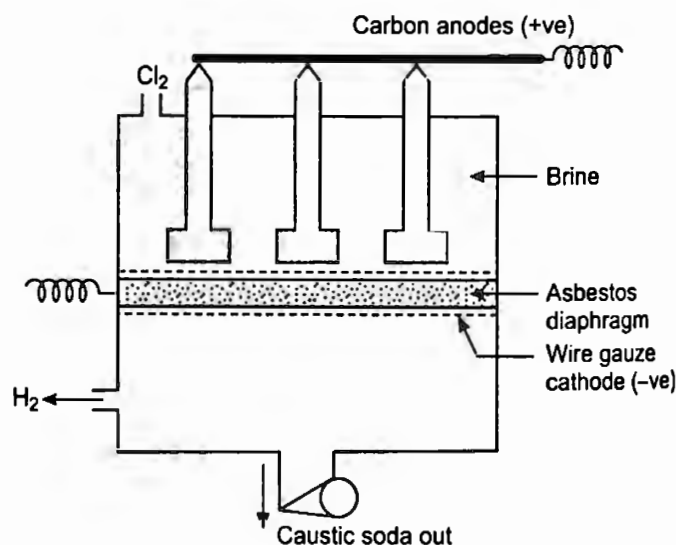
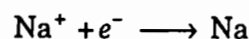


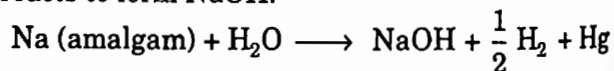
Fig. 8.4 A Diaphragm cell

## Mercury Cathode Cell (Castner-Kellner Cell)

During the electrolysis of brine,  $\text{Na}^+$  is discharged at cathode



If the cathode is made of mercury, the Na atoms produced are dissolved in mercury and form an amalgam. The amalgam is pumped to a different compartment and water reacts to form NaOH.



Originally the anodes were made of graphite, but because traces of oxygen are produced in a side reaction, they become pitted with corrosion. The anodes are now made of steel coated with titanium (Fig. 8.5).

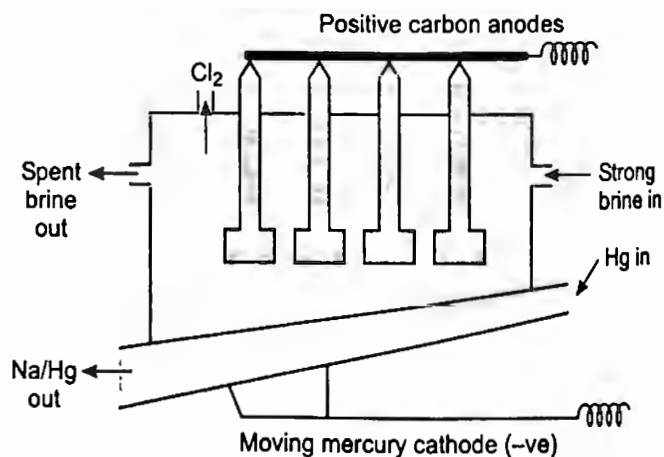
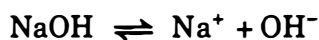


Fig. 8.5 The Castner-Kellner cells

## Properties

White crystalline deliquescent solid, highly soluble in water but sparingly in alcohol corrosive to skin. It breaks down the proteins of skin to a pasty mass hence called caustic soda.

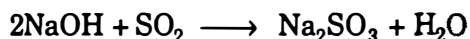
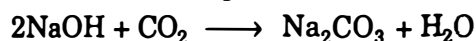
- A strong base ionised almost completely



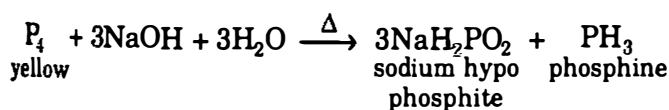
Equivalent weight of NaOH = molecular weight  
= 40 g equiv<sup>-1</sup>

## With Acidic Oxide

It can absorb  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{NO}_2$  etc. (acidic oxide) to form salt

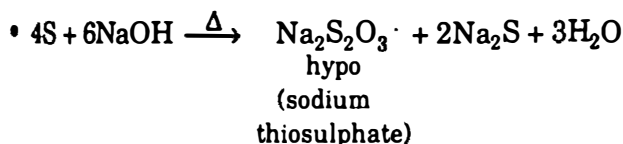


## With $\text{P}_4$



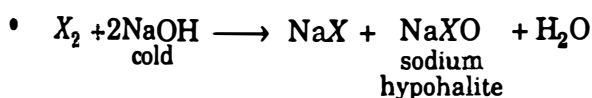
## With S

It is a disproportionation reaction of  $\text{P}_4$  to  $\text{H}_2\text{PO}_2^-$  (by oxidation) and  $\text{PH}_3$  (by reduction)

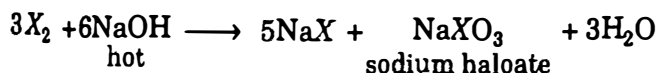


## With Halogens

$\text{X}_2$  ( $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ) disproportionates to  $\text{X}^-$  and  $\text{XO}^-$  in cold and dilute alkaline solution (NaOH)

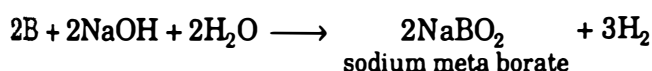
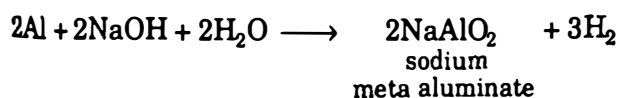
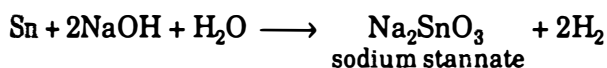
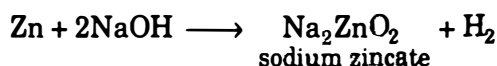


$\text{X}_2$  ( $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ) also disproportionates to  $\text{X}^-$  and  $\text{XO}_3^-$  in hot and concentrated alkaline solution (NaOH)



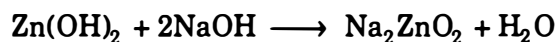
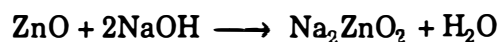
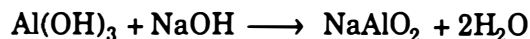
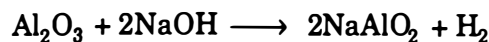
## With Metals

Elements like Zn, Al, Sn, B etc. liberate  $\text{H}_2$  with NaOH



## With Oxide

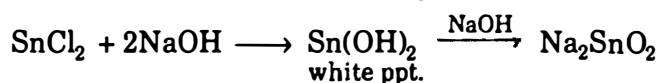
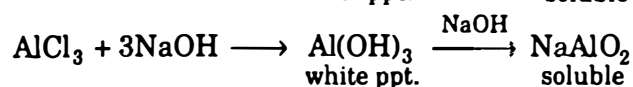
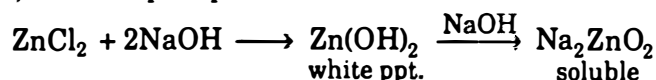
Amphoteric oxides (as well as hydroxides) dissolve in NaOH.



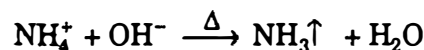
(similarly with  $\text{SnO}$ ,  $\text{PbO}$ )

## With Salts

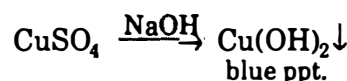
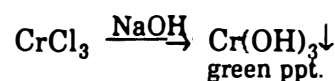
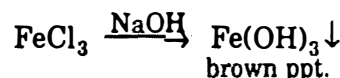
Salts like  $\text{ZnCl}_2$ ,  $\text{SnCl}_2$ ,  $\text{AlCl}_3$  etc. give white ppt with NaOH; however precipitate dissolves in excess of it.



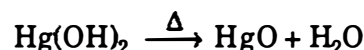
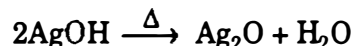
- $\text{NH}_4^+$  salts are decomposed by NaOH forming  $\text{NH}_3$



- Salts of transitional metals give insoluble hydroxide with NaOH.

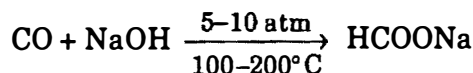


However,  $\text{AgOH}$  and  $\text{Hg}(\text{OH})_2$  decompose to oxide on heating.



## With CO

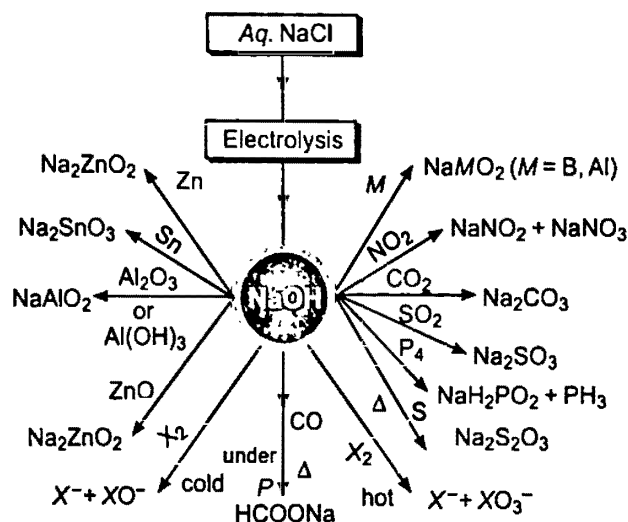
$\text{HCOONa}$  is formed when CO is passed into NaOH at high pressure and temperature



## Application

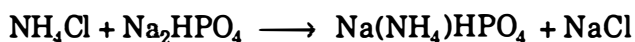
NaOH finds wide application in

- (1) paper industry
- (2) as a laboratory reagent.
- (3) alumina production
- (4) soap industry
- (5) rayon industry

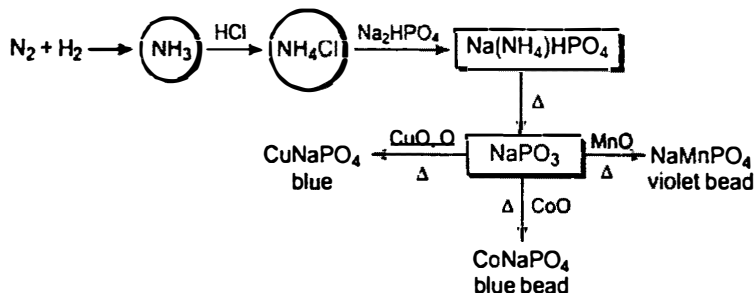
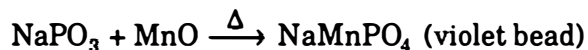


### Microcosmic Salt

- Colourless crystals of microcosmic salt are obtained when  $\text{NH}_4\text{Cl}$  and  $\text{Na}_2\text{HPO}_4$  in 1 : 1 molar ratio are dissolved in hot water and cooled.

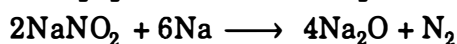
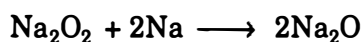
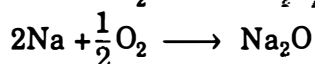
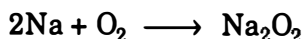


- On heating,  $\text{NaPO}_3$  is formed, which forms coloured beads of orthophosphates with oxides of transition metal and cloudy bead with  $\text{SiO}_2$ .



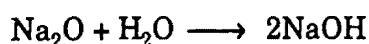
### Sodium Oxide and Peroxide

- Sodium peroxide along with sodium oxide is formed when sodium burns in air or with  $\text{NaNO}_2$ .



Oxone is a commercial name for the preparation of  $\text{Na}_2\text{O}_2$  that is used in breathing apparatus.

- $\text{Na}_2\text{O}$  is colourless ionic solid and aqueous solution is a strong base.

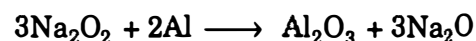


### DEEP Focus

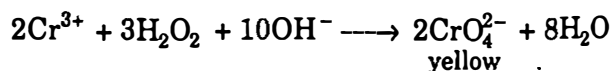
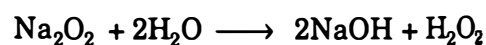
- $\text{Na}_2\text{O}_2$  is diamagnetic (all electrons paired) and is regarded as a salt of dibasic acid  $\text{H}_2\text{O}_2$ .  $\text{O}_2^{2-}$  is isoelectronic of  $\text{F}_2$   

$$\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{H}_2\text{O}_2$$
- $\text{Na}_2\text{O}_2$  is colourless in pure form but is pale yellow in colour due to presence of sodium superoxide  $\text{NaO}_2$  and is an oxidising agent.

– Al is oxidised to  $\text{Al}_2\text{O}_3$ .

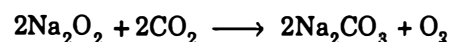
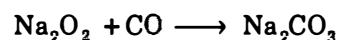


–  $\text{Cr}^{3+}$  salt is oxidised to  $\text{CrO}_4^{2-}$  (yellow).



### DEEP Focus

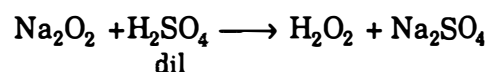
Because it reacts with  $\text{CO}_2$  in the air, it has been used to purify air in submarines and confined spaces, as it both removes  $\text{CO}_2$  and produces  $\text{O}_2$ .



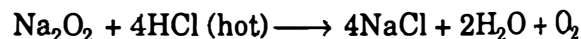
- $2\text{Na}_2\text{O} \xrightarrow{>400^\circ\text{C}} \text{Na}_2\text{O}_2 + 2\text{Na}$  (vapour)

In the absence of oxygen on oxidisable material, the peroxides (except  $\text{Li}_2\text{O}_2$ ) are stable towards, thermal decomposition up to quite high temperature ( $\text{Na}_2\text{O}_2 \approx 675^\circ\text{C}$ ).

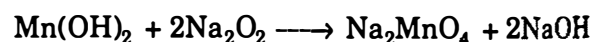
- $\text{Na}_2\text{O}_2$  gives  $\text{H}_2\text{O}_2$  with dil acids



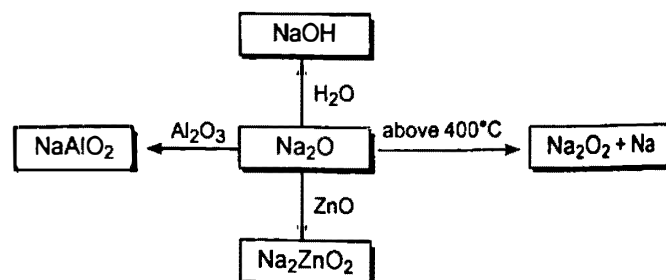
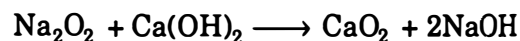
- $\text{O}_2$  is formed when  $\text{Na}_2\text{O}_2$  reacts with hot acids.

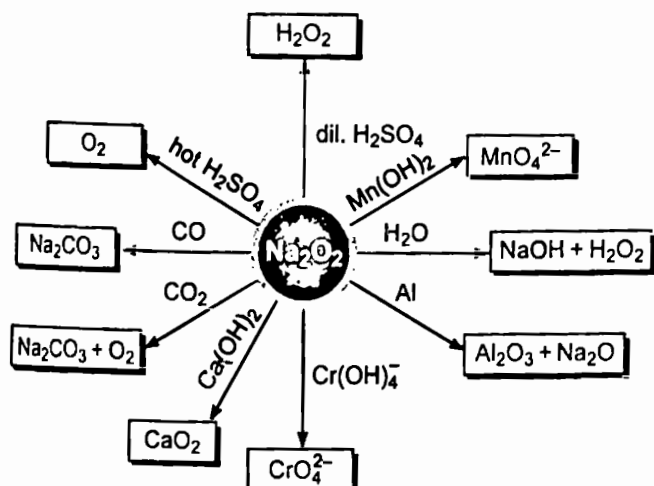


- $\text{Na}_2\text{O}_2$  oxidises  $\text{Mn}(\text{OH})_2$  to  $\text{MnO}_4^{2-}$  (green)



When mixture of  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{O}_2$  is compressed  $\text{CaO}_2$  is formed.





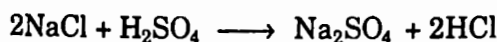
$O_2^{2-}$  has following MO electronic configuration  
 $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2$

$(\pi 2p_y)^2(\pi 2p_z)^2(\pi^* 2p_y)^2(\pi^* 2p_z)^2$

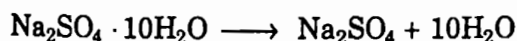
with bond-order one and diamagnetic (all electrons paired)

## Sodium Sulphate

Anhydrous sodium sulphate ( $Na_2SO_4$ ), called salt cake, is the by-product of HCl industry



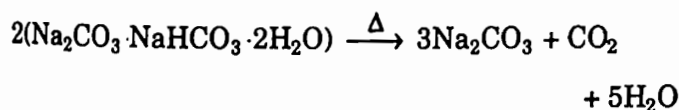
- If aqueous solution of  $Na_2SO_4$  is cooled below  $32^\circ C$ , Glauber's salt  $Na_2SO_4 \cdot 10H_2O$  separates. However, if cooling is done below  $12^\circ C$ ,  $Na_2SO_4 \cdot 7H_2O$  crystals are formed.
- In dry air  $Na_2SO_4 \cdot 10H_2O$  effloresces forming anhydrous  $Na_2SO_4$



- $Na_2SO_4$  finds use in paper industry, detergent and glass manufacture.

## Sodium Carbonate

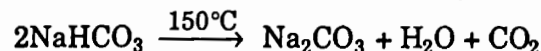
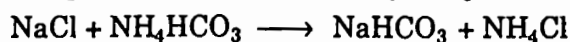
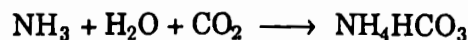
Since pre-historic times a natural deposit called Trona,  $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$  (sesqui-carbonate) has been obtained from dried-up lake beds in Egypt. Trona is sometimes called sodium sesqui-carbonate (sesqui means one and a half) and on heating it,  $Na_2CO_3$  is obtained.



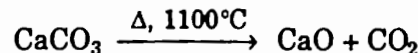
## The Solvay (ammonia-soda) process

- The Solvay (ammonia-soda) process is widely used to produce  $Na_2CO_3$  synthetically after Leblanc process proved non-economical.

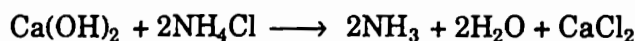
Reactions involved in the preparation of  $Na_2CO_3$  by the Solvay process are :



$CO_2$  is obtained by the decomposition of  $CaCO_3$



$CaO(aq)$  can decompose  $NH_4Cl$  to form  $NH_3$  which can be reused



Thus,  $NH_3$  is required in first instance only; it is recycled in further cycles. It is shown in the (Fig. 8.6 – 8.8).

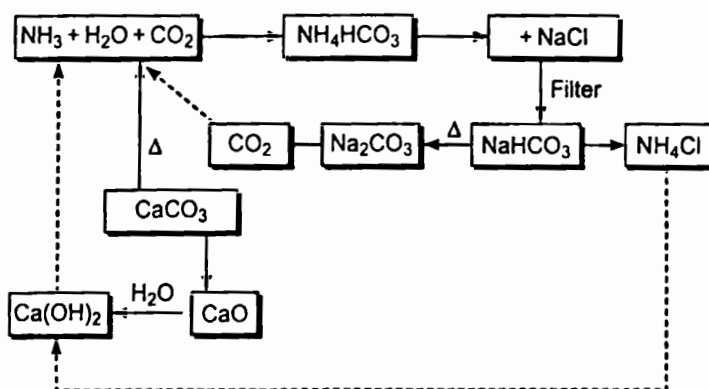


Fig. 8.6 Solvay process for the manufacture of  $Na_2CO_3$  (...) represents recycled process.

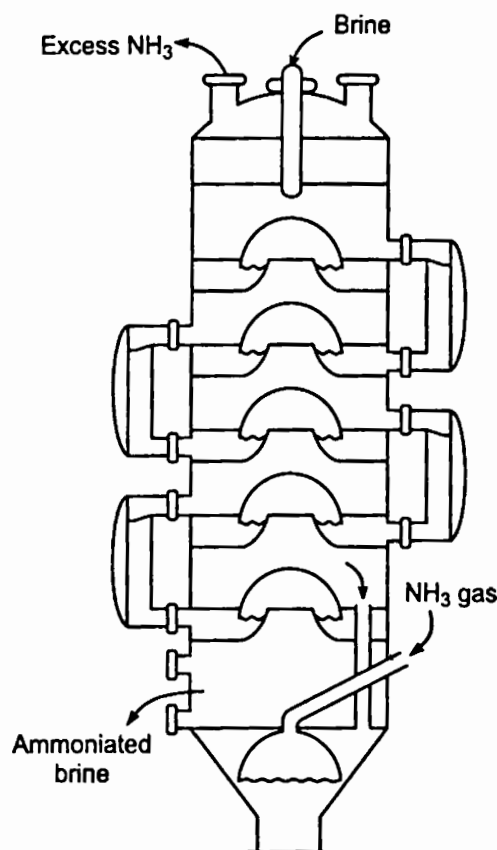


Fig. 8.7 The ammoniation of brine solution (Solvay process)



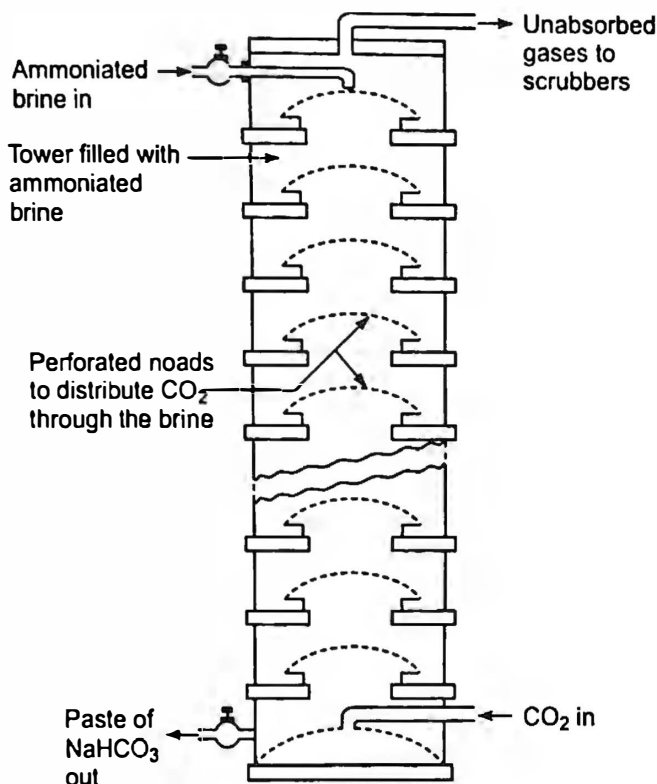
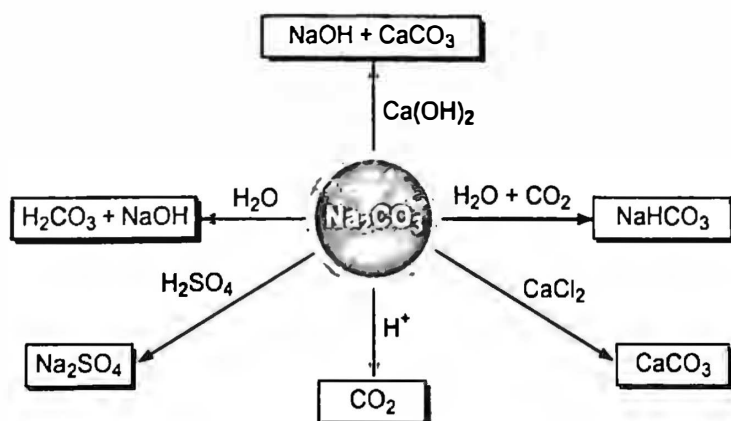


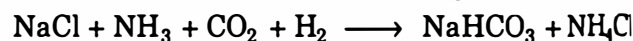
Fig. 8.8 Carbonating tower (Solvay process)

- $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  — washing soda widely used in soap and detergent
- $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$  — crystal carbonate / heavy ash  
 $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  widely used in glass sheets and glass-fibres manufacturing
- $\text{Na}_2\text{CO}_3$  — soda ash or light ash earlier used to prepare  $\text{NaOH}$ , and in petroleum refinery and textile industry
- $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  effloresces to anhydrous  $\text{Na}_2\text{CO}_3$ .  
$$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$$
- $\text{Na}_2\text{CO}_3$  is thermally stable and does not give  $\text{CO}_2$ .  
$$\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \longrightarrow 2\text{NaHCO}_3$$
  
$$\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 \longrightarrow 2\text{NaOH} + \text{CaCO}_3$$
- Aqueous solution is alkaline due to hydrolysis.  
$$\text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{NaOH} + \text{H}_2\text{CO}_3$$



## Sodium Bicarbonate (Baking Soda)

Sodium bicarbonate is the intermediate compound in the manufacture of sodium carbonate by the Solvay process, principal chemical reaction being:



- $\text{KHCO}_3$  can't be prepared by Solvay process,  $\text{KHCO}_3$  being highly soluble in water.
- $2\text{NaHCO}_3 \xrightarrow{50-100^\circ\text{C}} \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$

Due to this property of giving  $\text{CO}_2$  on gentle heating  $\text{NaHCO}_3$  finds use in

- Baking powder (which contains  $\text{NaHCO}_3$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and starch). Improved baking powder contains 40% starch, 30%  $\text{NaHCO}_3$ , 20%  $\text{NaAl}(\text{SO}_4)_2$  and 10%  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ .
- Pharmaceutical products (including antacid preparation for indigestion)
- Fire extinguishers.
- $\text{NaHCO}_3$  is also added in small amount to table salt ( $\text{NaCl}$ ).  $\text{NaCl}$  is often contaminated with small amount of  $\text{MgCl}_2$  which being hygroscopic makes  $\text{NaCl}$  moist. Adding  $\text{NaHCO}_3$  converts  $\text{MgCl}_2$  to  $\text{MgCO}_3$  which is non-hygroscopic salt.  
$$\text{MgCl}_2(\text{s}) + 2\text{NaHCO}_3(\text{s}) \longrightarrow \text{MgCO}_3(\text{s}) + 2\text{NaCl}(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$$

- It is amphoteric:  $\text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3$   
$$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$$

Amphoteric species is  $\text{H}^+$  ion donor (acid) and  $\text{H}^+$  ion acceptor (base).

## Compounds of Potassium

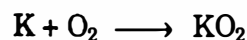
Potassium compounds occur in the earth's crust especially as silicates. All land plants contain considerable amounts of potassium salts due to absorption from the soil. Deficiency of the potassium salts in soil is made up by adding potassium fertilizers.

Potassium can also be made by electrolysis of molten  $\text{KCl}$ . But molten potassium is soluble in molten  $\text{KCl}$  and thus separation of metal is difficult. The preferred method for preparation of potassium uses the reaction of sodium vapour with molten  $\text{KCl}$ , with potassium being continually removed from the equilibrium mixture

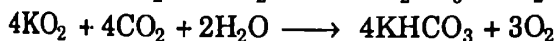
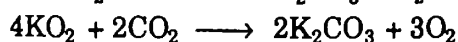
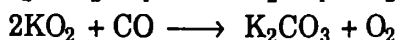
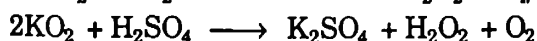
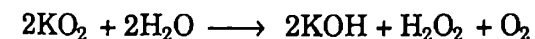


## Potassium Superoxide

- It is formed as a chrome-yellow (orange) powder by burning potassium in excess of moisture-free oxygen or air.

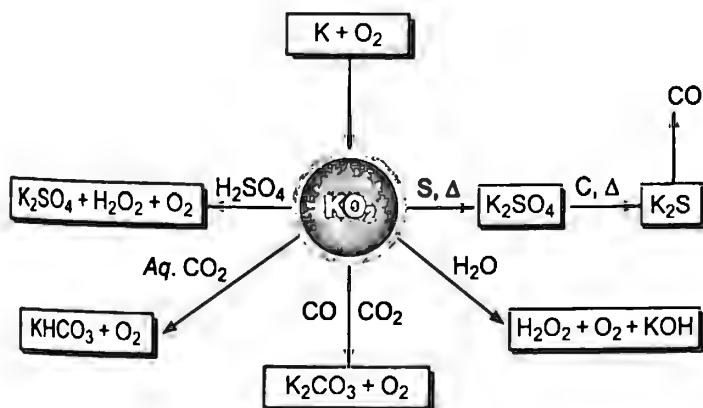


- $\text{KO}_2$  is better (than  $\text{K}_2\text{O}_2$ ) oxidising agent since it produces  $\text{O}_2$  and  $\text{H}_2\text{O}_2$  both in aqueous or acidic solution



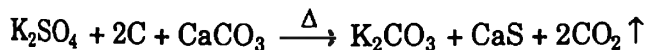
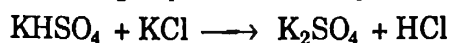
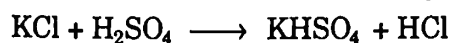
$\text{KO}_2$  thus finds applications to be used in space capsules, submarines and breathing masks, because it both produces  $\text{O}_2$  and removes  $\text{CO}_2$  and  $\text{CO}$ . Both functions are important in life support system.

- The superoxide contains  $\text{O}_2^-$  ion, which has an unpaired electron and hence, it is paramagnetic. Bond order is 1.5

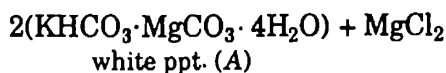
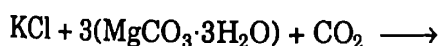


### Potassium Carbonate (Potash or Pearl Ash)

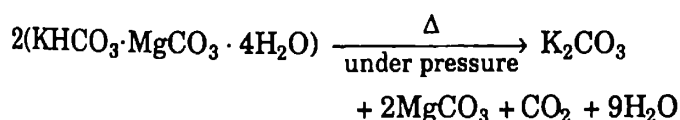
- Solvay process is not adopted to prepare  $\text{KHCO}_3$  (or  $\text{K}_2\text{CO}_3$ ) being highly water soluble.
- Leblanc process involves conversion of  $\text{KCl}$  (from carnallite) first into  $\text{K}_2\text{SO}_4$  and then heating it ( $\text{K}_2\text{SO}_4$ ) with carbon and limestone ( $\text{CaCO}_3$ ).



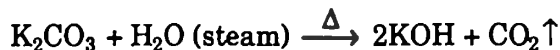
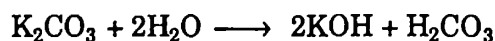
- Magnesia process (also called Precht's process) involves passing of  $\text{CO}_2$  into aqueous solution of  $\text{KCl}$  and  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  at  $17^\circ\text{C}$ , when a double salt  $\text{KHCO}_3 \cdot \text{MgCO}_3 \cdot 4\text{H}_2\text{O}$  is precipitated.



- Precipitate (A) on heating under pressure gives a mixture of  $\text{K}_2\text{CO}_3$  (soluble) and  $\text{MgCO}_3$  (insoluble) and thus separated.  $\text{MgCO}_3$  is reused in further preparation.



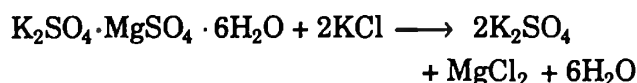
- Colourless deliquescent powder soluble in water (more than  $\text{Na}_2\text{CO}_3$  and  $\text{Li}_2\text{CO}_3$ ).
- Aqueous solution is alkaline due to hydrolysis.



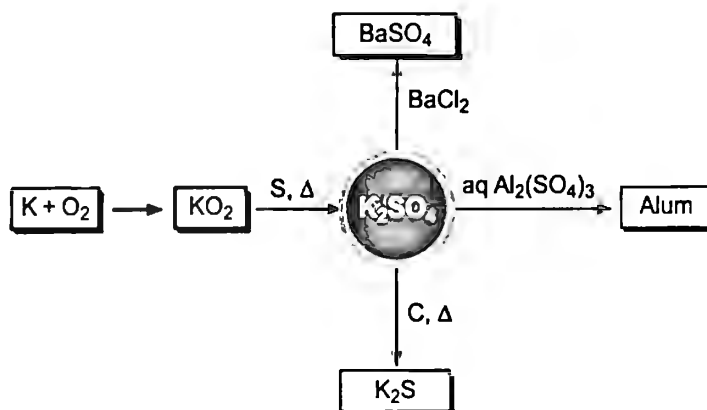
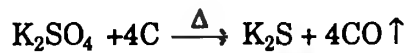
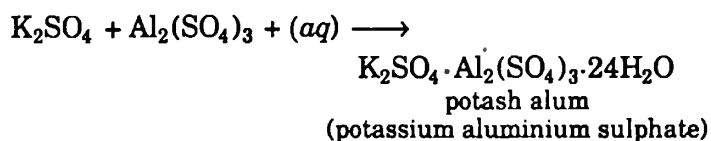
$\text{K}_2\text{CO}_3$  finds wide use in the manufacture of soft soap, and is washing wool.

### Potassium Sulphate

- A naturally occurring mineral, Schonite —  $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  is treated with  $\text{KCl}$  in aqueous solution and colourless anhydrous crystals of  $\text{K}_2\text{SO}_4$  separate.



- It is highly soluble in  $\text{H}_2\text{O}$  and forms double salts like potash alum



### Potassium Nitrate

$\text{NaNO}_3$  (chile saltpeter) is converted to  $\text{KNO}_3$  by following exchange reaction :



Above reaction is spontaneous in forward side as,  $\text{NaCl}$  being less soluble than  $\text{KNO}_3$ , is removed by crystallisation, and  $\text{KNO}_3$  remains in solution, and can be obtained by evaporation of water.  $\text{KNO}_3$  is used in gun powder (a mixture of sulphur, carbon and  $\text{KNO}_3$ )



## Diagonal Relationship

### —Anomalous Behaviour of Lithium

The first element of a group in many ways differs from the other heavier members of the group. These differences arise on account of three factors :

- the small size
- the high electronegativity, and
- the unavailability of *d*-orbitals among the first row elements (Li to F).

Its polarising power (*i.e.*, charge/radius ratio) is the greatest of all the alkali metal ions. This results in increased covalent character of lithium compounds which is responsible for their solubility in organic solvents.

Due to the very small size of lithium, the metallic bonding between the atoms in the metallic lattice is very strong giving rise to strong cohesive forces. This is shown in its relatively higher melting and boiling points, hardness and homonuclear bond energy.

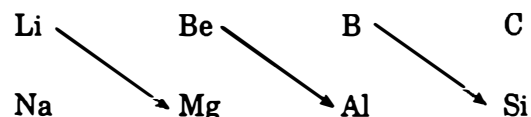
The relatively higher attraction of lithium for its outer electron results in its relatively higher electronegativity, ionisation energy, hydration energy, electron affinity and of course smaller atomic radii relative to the other homologues.

Similar anomalies are also found in the chemical properties but the differences appear greater.

- Lithium salts of large polarisable anions are thermally less stable than those of other alkali metals, *e.g.*, lithium carbonate decomposes at 950 K, whereas no decomposition of sodium carbonate take place above 1050 K.
- Lithium forms no solid bicarbonate, triiodide and superoxide as these are unstable at room temperature, whereas those of other alkali metals require a higher temperature to affect their decomposition.
- Lithium salts of anions of high charge density are less soluble than those of other alkali metals. The halides of lithium are more covalent than the other halides and are more soluble in organic solvents.
- Lithium forms stable salts with anions of high charge density owing to their high lattice energy. For example, in air, lithium forms the normal oxide, whereas the others form higher oxides. Lithium reacts with nitrogen to form nitride,  $\text{Li}_3\text{N}$ , the others do not react. Lithium hydride is more stable than the other hydrides and lithium carbide is formed more easily with acetylene.
- Lithium reacts slowly with water.

- Lithium forms more stable covalent bonds than other alkali metals and, therefore, forms more stable complex compounds. For example, lithium cannot be recovered unchanged from its liquid ammonia solution, owing to the formation of  $[\text{Li}(\text{NH}_3)_4]^+$ .

The first element of group often shows resemblance to the second element of the neighbouring group on the right. This type of behaviour is known as **diagonal relationship**.



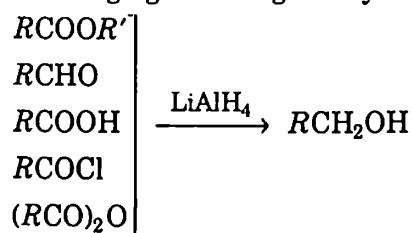
This similarity between Li and Mg is particularly striking and arises because of their similar ionic sizes ( $\text{Li}^+ = 76 \text{ pm}$ ;  $\text{Mg}^{2+} = 72 \text{ pm}$ ). The ionic potentials (charge/size ratio) are very similar for the pair Li and Mg.

Li and Mg show close resemblance in the following:

|                             |                                                                                                                                                                                                                                                                                                                                                                                                                                       |
|-----------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Nitrides                    | Li and Mg both form nitrides. Other alkali metals do not.<br>$6\text{Li} + \text{N}_2 \xrightarrow{\Delta} 2\text{Li}_3\text{N}$ $3\text{Mg} + \text{N}_2 \xrightarrow{\Delta} \text{Mg}_3\text{N}_2$                                                                                                                                                                                                                                 |
| Carbonates and bicarbonates | Like $\text{MgCO}_3$ , $\text{Li}_2\text{CO}_3$ is decomposed by heat (the other alkali carbonates are thermally stable). Both carbonates are insoluble while $\text{Na}_2\text{CO}_3$ , $\text{K}_2\text{CO}_3$ are soluble.<br>$\text{MgCO}_3 \xrightarrow{\Delta} \text{MgO} + \text{CO}_2$ $\text{Li}_2\text{CO}_3 \longrightarrow \text{Li}_2\text{O} + \text{CO}_2$<br>Solid bicarbonates of lithium and magnesium do not exist |
| Nitrates                    | $\text{LiNO}_3$ decomposes to give $\text{Li}_2\text{O}$ like $\text{Mg}(\text{NO}_3)_2$ , but other alkali metal nitrates give nitrite.<br>$\text{Mg}(\text{NO}_3)_2 \xrightarrow{\Delta} \text{MgO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2$ $2\text{LiNO}_3 \xrightarrow{\Delta} \text{Li}_2\text{O} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2$ $2\text{NaNO}_3 \longrightarrow 2\text{NaNO}_2 + \text{O}_2$                           |
| Oxides                      | Both give their normal oxides, $\text{Li}_2\text{O}$ , $\text{MgO}$ , when they burn in oxygen; peroxides and superoxides are not formed. Na forms peroxide, $\text{Na}_2\text{O}_2$ while K forms superoxide, $\text{KO}_2$ .                                                                                                                                                                                                        |
| Chlorides                   | Both chlorides are hydrated, $\text{LiCl} \cdot 2\text{H}_2\text{O}$ , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . both are deliquescent and anhydrous salts are soluble in ether.                                                                                                                                                                                                                                                    |
| Phosphates                  | Solubility of both Li and Mg phosphate is low.                                                                                                                                                                                                                                                                                                                                                                                        |
| Fluorides                   | $\text{LiF}$ and $\text{MgF}_2$ are sparingly soluble in water.                                                                                                                                                                                                                                                                                                                                                                       |
| Hydration                   | Both $\text{Li}^+$ and $\text{Mg}^{2+}$ are heavily hydrated.                                                                                                                                                                                                                                                                                                                                                                         |
| Hydroxide                   | $\text{LiOH}$ , $\text{Mg}(\text{OH})_2$ both are weak bases and very slightly soluble in water, and their hydroxides decompose on heating.                                                                                                                                                                                                                                                                                           |
| Perchlorates                | Lithium perchlorate ( $\text{LiClO}_4$ ) and magnesium perchlorate [ $\text{Mg}(\text{ClO}_4)_2$ ] both are extremely soluble in alcohol and used as water absorber.                                                                                                                                                                                                                                                                  |
| Alkyl and aryl              | Li alkyls and aryls are important in organic syntheses and Grignard reagent ( $\text{RMgX}$ )                                                                                                                                                                                                                                                                                                                                         |

## Uses of Alkali Salts

- Lithium stearate is used as a thickener and gelling agent to transform oils into lubricating greases.
- Lithium hydride (LiH) is used to generate hydrogen in military, meteorological, and other applications.
- $\text{LiAlH}_4$  is a reducing agent in organic synthesis.



- $\text{Li}_2\text{CO}_3$  when taken orally provides an effective treatment for manic-depressive psychoses.
- $\text{Li/FeS}_x$  battery systems are emerging as a potentially viable energy storage system and as a non-polluting silent source of power for electric cars.
- $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$  find applications in soap, paper and glass industry and as reagent in the laboratory.
- $\text{K}_2\text{CO}_3$  is used chiefly in high-quality decorative glassware, in optical lenses, colour TV tubes and

fluorescent lamps; it is also used in china wares, textile dyes and pigments.

- $\text{KNO}_3$  is a powerful oxidising agent and mainly used in gunpowders and pyrotechnics, and in fertilizers.
- $\text{KMnO}_4$  is used as an oxidiser, decolourisers, bleacher and purification agent; its major application is in the manufacture of saccharin.
- $\text{KO}_2$  is used in breathing apparatus as an auxiliary supply of  $\text{O}_2$  in mines, submarines and space vehicles.
 
$$4\text{KO}_2 + 2\text{CO}_2 \longrightarrow 2\text{K}_2\text{CO}_3 + 3\text{O}_2$$

$$4\text{KO}_2 + 4\text{CO}_2 + 2\text{H}_2\text{O} \longrightarrow 4\text{KHCO}_3 + 3\text{O}_2$$
- $\text{KClO}_3$  is used in matches and explosive.
- $\text{KBr}$  in photography and as a source of  $\text{Br}_2$  in organic synthesis.
- $\text{Na}_2\text{O}_2$  finds widespread use as a bleaching agent for fabrics, paper pulp wood etc.
- $\text{Li}$  is used in batteries and alloys.
- $\text{K}$  is used for analytical reagents because  $\text{K}^+$  salts not so highly solvated as those of  $\text{Na}^+$ , making it easier to obtain anhydrous reagents.
- $\text{Cs}$  is used in photocells because of its low ionisation energy.

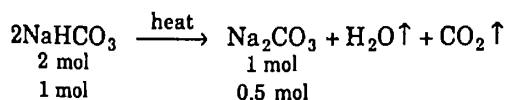
## Target Practice 2

- Mixture containing one mole  $\text{Na}_2\text{CO}_3$  and one mole  $\text{NaHCO}_3$  is heated. What is amount (in moles) of the residue? .....
- Table salt is always contaminated with  $\text{NaHCO}_3$ . It is to .....
- $\text{NaOH}$  is prepared industrially by electrolysis of brine ( $\text{NaCl}$ )
 
$$2\text{NaCl}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{Cl}_2(\text{g}) + 2\text{NaOH}(\text{aq}) + \text{H}_2(\text{g})$$
 What is the name of this process? .....

- In United States, sodium carbonate is obtained from naturally occurring deposits of the mineral trona. Write formula of trona. ....
- How can you stabilise solutions containing  $\text{Na}^+$ ? .....
- Name oxides of alkali metals which are
  - paramagnetic in nature .....
  - binary salt .....
  - used in life saving devices .....
  - diamagnetic .....

## Answers

- $\text{Na}_2\text{CO}_3 \xrightarrow{\text{heat}}$  no effect. Thus, residue is 1 mol  $\text{Na}_2\text{CO}_3$



Residue is 0.5 mol  $\text{Na}_2\text{CO}_3$ . Thus total residue is 1.5 mol  $\text{Na}_2\text{CO}_3$ .

- Table salt  $\text{NaCl}$  has also  $\text{MgCl}_2$  as impurity (from sea). The magnesium salt is hygroscopic; that is it picks water up from the air and thus  $\text{NaCl}$  becomes wet. If  $\text{NaHCO}_3$  is added to table salt, it converts  $\text{MgCl}_2$  to  $\text{MgCO}_3$  which is non-hygroscopic salt.

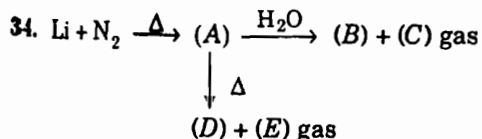


- Soda-lime process
- $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$
- Larger anion as  $\text{O}_2^-$  (superoxides) can stabilise  $\text{Na}^+$ .  
 $\text{NaO}_2$  is stable.
- (a)  $\text{KO}_2$  (due to  $\text{O}_2^-$ )  
(b)  $\text{KO}_2$   
(c)  $\text{Na}_2\text{O}_2$   
(d)  $\text{Na}_2\text{O}_2$

## Practice Exercise 2

- What is the nature of CO when it reacts with NaOH?
- Gas (A) + NaOH  $\longrightarrow$  (B)  $\xrightarrow{\Delta}$  (C)  $\xrightarrow{H^+}$  (D)  
 $\downarrow$  CaCl<sub>2</sub>  
 white ppt (E)  
 (C) and (D) both decolourise acidified KMnO<sub>4</sub>.  
 Identify (A), (B), (C) and (D) and explain reactions.
- (A) gives white ppt with AgNO<sub>3</sub> soluble in aq NH<sub>3</sub>. (A) gives green ppt (B) with NaOH but ppt dissolves to yellow solution (C) when heated with H<sub>2</sub>O<sub>2</sub>. (C) gives yellow ppt (D) with BaCl<sub>2</sub>. What are (A), (B), (C) and (D)?
- (A) gives white ppt (B) with NaOH, but (B) dissolves in excess of NaOH forming (C). (C) gives white ppt (D) when H<sub>2</sub>S gas is passed into it. (A) also gives white ppt (E) with BaCl<sub>2</sub>. (E) is insoluble in conc. HNO<sub>3</sub>. Identify (A), (B), (C), (D) and (E).
- PbO<sub>2</sub> is soluble in NaOH and also in HCl. What does it reflect about the nature of PbO<sub>2</sub>?
- A mixture contains Cr<sup>3+</sup> and Zn<sup>2+</sup> salts. How will you separate and analyse them?
- Colourless salt (A)  $\xrightarrow{NaOH, \Delta}$  (B) (gas)  
 $\downarrow$  CaCl<sub>2</sub> solution  
 white ppt (C)  
 (B) gives white fumes with HCl.  
 (C) decolorises acidified KMnO<sub>4</sub>.  
 What is (A)? Explain reactions.
- If NaOH solution is placed in an open vessel, will there be any change in its weight? Explain.
- What is difference in the chemistry of microcosmic bead test and borax bead test?
- H<sub>3</sub>PO<sub>4</sub> + 2NaOH  $\longrightarrow$  (A)  $\xrightarrow{NH_4Cl}$  (B)  $\longrightarrow$  (C)  
 $\xrightarrow{(E) \Delta}$  Violet bead  
 (E) is obtained along with gas (F) when (D) is heated. Gas (F) turns lime water milky and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/H<sup>+</sup> solution green. What are (A), (B), (C), (D), (E) and (F) and explain reactions.
- Sodium oxide solution can't be stored in Zn or Al vessel. Explain.
- There is white deposit in a glass vessel in which NaOH is stored. Explain.
- What do you consider about Na<sub>2</sub>O<sub>2</sub>, a salt of monobasic acid or a salt of dibasic acid?
- How will you make distinction between Na<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>O?
- Sodium forms two oxides (A) and (B) having 25.81% and 41.03% oxygen respectively. What is reaction of (A) and (B) with  
 (a) H<sub>2</sub>O      (b) H<sub>2</sub>SO<sub>4</sub>      (c) Cr(OH)<sub>3</sub>      (d) MnO<sub>2</sub>
- Sodium superoxide NaO<sub>2</sub> can't be prepared directly from sodium, but from Na<sub>2</sub>O<sub>2</sub>. Write balanced chemical equation. How much of Na<sub>2</sub>O<sub>2</sub> is required to prepare 11 g of NaO<sub>2</sub>?
- Fill in the blanks :  
 1. Na<sub>2</sub>O has ..... structure.
- Bond orders of O<sub>2</sub><sup>2-</sup>, O<sub>2</sub><sup>-</sup>, O<sub>2</sub> are respectively ..... and .....
- Na<sub>2</sub>O<sub>2</sub> is .....absorber and ..... producer and is thus used in .....
- What happens when equimolar quantity of Na<sub>2</sub>SO<sub>4</sub> and conc. H<sub>2</sub>SO<sub>4</sub> is cooled?
- Na<sub>2</sub>SO<sub>4</sub> + carbon  $\longrightarrow$  (A)  $\xrightarrow{Na_2[Fe(CN)_5NO]}$  (B) (purple)  
 $\downarrow$  CdCO<sub>3</sub>  
 yellow ppt (C)  
 Identify (A), (B) and (C).
- A colourless salt (X) has 50% Na<sub>2</sub>SO<sub>3</sub> and 50% H<sub>2</sub>O. What is the formula of (X)? How much of SO<sub>2</sub> at NTP is obtained when 2.52 g of (X) reacts with excess of dil. H<sub>2</sub>SO<sub>4</sub>?
- Na<sub>2</sub>CO<sub>3</sub> is widely used in softening of hard water. If 1 L of hard water required 0.0106 g of Na<sub>2</sub>CO<sub>3</sub>, calculate hardness in ppm (parts per million i.e., 10<sup>6</sup> mL) of CaCO<sub>3</sub>.
- Silver can be extracted from silver coin and Na<sub>2</sub>CO<sub>3</sub> is used in one of the steps. Outline the extraction process.
- 3 moles of mixture of NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> is strongly heated at 200°C, when 1 mole of CO<sub>2</sub> is obtained. What is the weight of residue? What is molar percentage of NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> in the mixture?
- Baking powder is said to contain NaHCO<sub>3</sub>, Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>, starch and NaAl(SO<sub>4</sub>)<sub>2</sub>. What is the function of each content?
- Fire extinguisher contains NaHCO<sub>3</sub> and the compound (X). What is the compound (X)? Explain.
- Arrange the following in increasing solubility in water.  
 (i) LiOH, NaOH, KOH  
 (ii) Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>  
 (iii) LiHCO<sub>3</sub>, NaHCO<sub>3</sub>, KHCO<sub>3</sub>  
 (iv) LiCl, NaCl, KCl
- What is the formula of the three oxides of potassium with percentage of oxygen being  
 (A) : 17.02%      (B) : 29.09%  
 (C) : 45.07%  
 Which of them will show paramagnetism?
- Which is most thermally stable out of Li<sub>2</sub>CO<sub>3</sub>, MgCO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>?
- 1 mole of mixture of Li<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> on strongly heating gave 0.25 mole of CO<sub>2</sub>. What is mole % of each in the mixture?
- Which indicator, phenolphthalein or methyl orange will you choose in the titration of K<sub>2</sub>CO<sub>3</sub> solution with HCl?
- Identify (A) to (C) in the following :  
 $KO_2 + S \xrightarrow{\Delta} (A) \xrightarrow{BaCl_2} (B)$   
 $\downarrow$  Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution  
 (C)
- 10 mL of a solution of K<sub>2</sub>SO<sub>4</sub> on reaction with BaCl<sub>2</sub> gave 0.233 g of white ppt. What is concentration of K<sub>2</sub>SO<sub>4</sub> solution?  
 (Ba = 137, S = 32, O = 16, K = 39)

33. A gaseous mixture contains  $N_2$ ,  $O_2$  and  $CO_2$ . It is passed over heated Mg, then over heated Cu and finally into aqueous KOH. What happens?



What are (A), (B), (C), (D) and (E)?

35. Compare  $Li^+$  and  $Na^+$  salts in terms of  
(a) formation of ionic carbide

(b) complex formation

(c) solubility of  $CO_3^{2-}$ ,  $PO_4^{3-}$  and  $F^-$  in  $H_2O$

(d) nature of  $Cl^-$

(e) nature of bicarbonate

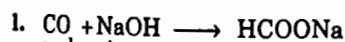
36. Sodium does not form carbide  $Na_2C_2$  with carbon but  $Na_2C_2$  can be formed by other source. What can be it?

37. Which is more stable out of

(i)  $Li_2O$  and  $Li_2CO_3$

(ii)  $Na_2O$  or  $Na_2CO_3$

## Answers

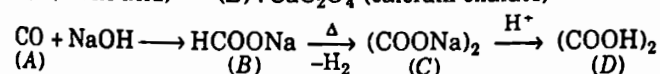


acid base  
CO is acidic oxide in this reaction.

2. (A) : CO (B) : HCOONa (sodium formate)

COONa  
(C) :  $\begin{array}{c} COONa \\ | \\ COONa \end{array}$  (sodium oxalate)

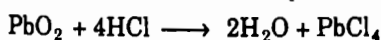
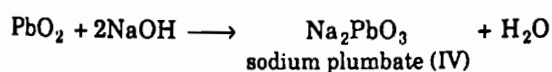
(D) : (oxalic acid) (E) :  $CaC_2O_4$  (calcium oxalate)



3. (A) :  $CrCl_3$  (B) :  $Cr(OH)_3$  (C) :  $Na_2CrO_4$  (D) :  $BaCrO_4$

4. (A) :  $ZnSO_4$  (B) :  $Zn(OH)_2$  (C) :  $Na_2ZnO_2$  (D) :  $ZnS$   
(E) :  $BaSO_4$

5.  $PbO_2$  is an amphoteric oxide



6.  $Cr^{3+} + Zn^{2+} \xrightarrow{(i) NaOH, \text{ excess}} \text{green ppt. } Cr(OH)_3 \downarrow$   
 $\xrightarrow{(ii) \text{ filter}} \downarrow$

$Na_2ZnO_2$  (soluble)



ZnS (white ppt)

$NaOH, H_2O_2$



$Na_2CrO_4$   
soluble (yellow)

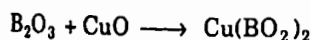
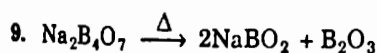
$(CH_3COO)_2Pb$

$CH_3COOH$

$PbCrO_4$  (yellow ppt)

7. (A) :  $(NH_4)_2C_2O_4$  (B) :  $NH_3$  (C) :  $CaC_2O_4$

8. NaOH absorbs  $CO_2$  from atmosphere hence weight of the solution would increase.

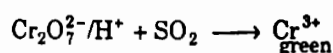
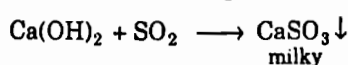


In the case of borax-bead test we take borax when coloured bead of the type  $Cu(BO_2)_2$  is formed.

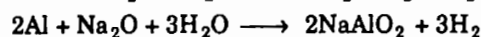
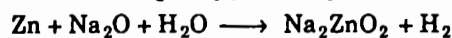
In case of microcosmic bead test, we take microcosmic salt.

10. (A) :  $Na_2HPO_4$  (B) :  $Na(NH_4)HPO_4$  (C) :  $NaPO_3$

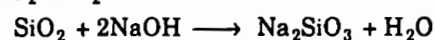
(D) :  $MnSO_3$  (E) :  $MnO$  (F) :  $SO_2$



11. Zn or Al reacts with  $Na_2O$  (aq), (actually with NaOH)

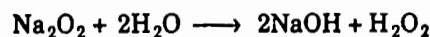


12. Glass has  $SiO_2$ .  $SiO_2$  reacts with NaOH.

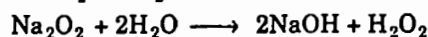
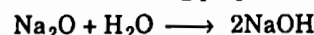


$Na_2SiO_3$  appears as white deposit.

13.  $Na_2O_2$  is a salt of dibasic acid  $H_2O_2$  which is formed on reaction with  $H_2O$ .

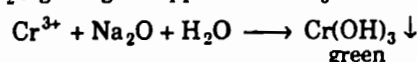


14.  $Na_2O$  does not show oxidising properties while  $Na_2O_2$  gives

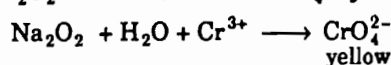


Add  $Cr^{3+}$  salt into aqueous solution of each

—  $Na_2O$  gives green ppt of  $Cr(OH)_3$

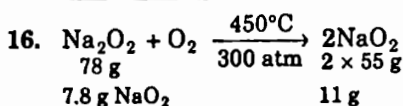


—  $Na_2O_2$  oxidises  $Cr^{3+}$  into  $CrO_4^{2-}$  (yellow)



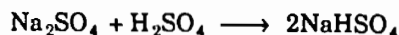
|           | A     |       | B     |       |
|-----------|-------|-------|-------|-------|
|           | O     | Na    | O     | Na    |
| 15.       | 25.81 | 74.19 | 41.03 | 58.97 |
| Mol ratio | 1.61  | 3.22  | 2.56  | 2.56  |
|           | 1 : 2 |       | 1 : 1 |       |

| A                                                      |  | B                                                                     |  |
|--------------------------------------------------------|--|-----------------------------------------------------------------------|--|
| $Na_2O$                                                |  | $Na_2O_2$                                                             |  |
| (a) $Na_2O + H_2O \longrightarrow 2NaOH$               |  | (a) $Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$                  |  |
| (b) $Na_2O + H_2SO_4 \longrightarrow 2Na_2SO_4 + H_2O$ |  | (b) $Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$             |  |
| (c) $Na_2O + Cr(OH)_3 \longrightarrow$<br>no effect    |  | (c) $Cr(OH)_3 + Na_2O_2 + H_2O \longrightarrow Na_2CrO_4$<br>(yellow) |  |
| (d) $Na_2O + MnO_2 \longrightarrow$<br>no effect       |  | (d) $Na_2O_2 + MnO_2 + H_2O \longrightarrow Na_2MnO_4$<br>(green)     |  |
|                                                        |  | $Na_2O_2$ is oxidant in (c) and (d) due to $H_2O_2$ .                 |  |



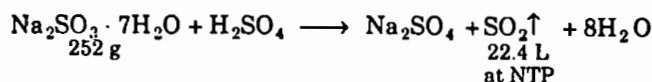
17. (1) antiferite (2) 1, 1.5 and 2 (3)  $CO_2$ ,  $O_2$ , submarines

18. Prism type crystals of
- $\text{NaHSO}_4$
- are formed.



19. (A) :
- $\text{Na}_2\text{S}$
- (B) :
- $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NOS}]$
- (C) :
- $\text{CdS}$

20. (X) :
- $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$



$\text{SO}_2$  : 0.224 L at NTP from 2.52 g  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ .

- 21.
- $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl}$

106 g      100 g

0.0106 g    0.010 g in 1 L (1000 mL) water

$$\frac{0.016 \times 10^6}{10^3} \text{ g in } 10^6 \text{ mL H}_2\text{O (ppm)}$$

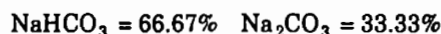
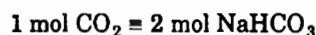
10 ppm  $\text{CaCO}_3$

22. Silver coin  $\xrightarrow[\text{HNO}_3]{\text{boil with}}$   $\text{AgNO}_3 + \text{Cu}(\text{NO}_3)_2$  etc.  $\xrightarrow{\text{NaCl}}$   $\text{AgCl} \downarrow$   
(other remain soluble)  
 $\xrightarrow{\text{Na}_2\text{CO}_3}$   $\text{Ag}_2\text{CO}_3 \downarrow \xrightarrow{\Delta}$   $\text{Ag}$

- 23.
- $2\text{NaHCO}_3 \xrightarrow{\Delta} \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \uparrow + \text{CO}_2 \uparrow$



$\text{CO}_2$  is due to  $\text{NaHCO}_3$  only



residue = 1 mol  $\text{Na}_2\text{CO}_3$  (in mixture)

+ 1 mol  $\text{Na}_2\text{CO}_3$  (from 2 mol  $\text{NaHCO}_3$ )

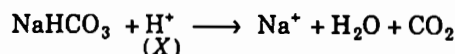
= 2 mol  $\text{Na}_2\text{CO}_3$  ( $\text{H}_2\text{O}$  and  $\text{CO}_2$  escape at  $200^\circ\text{C}$ )

24.  $\text{NaHCO}_3$  }  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  is acidic in aqueous solution.  
 $\text{Ca}(\text{H}_2\text{PO}_4)_2$  } acidic solution of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  liberates  $\text{CO}_2$   
 on reaction with  $\text{NaHCO}_3$

starch ] as a filler

$\text{NaAl}(\text{SO}_4)_2$  retarder so that  $\text{CO}_2$  is given off more slowly while preparing cake or bread.

25. Fire extinguisher contains
- $\text{NaHCO}_3$
- and compound X can be an acid (like
- $\text{CH}_3\text{COOH}$
- ) that can decompose
- $\text{NaHCO}_3$
- to give
- $\text{CO}_2$
- .



$\text{NaHCO}_3$  and acid (X) are in a sealed flask (but placed inside separately). in case of emergency (when there is fire), seal is

broken and X and  $\text{NaHCO}_3$  react instantly to give  $\text{CO}_2$  which can put off fire.

26. In all cases compound of
- $\text{Li}^+$
- ,
- $\text{Na}^+$
- and
- $\text{K}^+$
- have solubility in the order :



27. (A) :
- $\text{K}_2\text{O}$
- (B) :
- $\text{K}_2\text{O}_2$
- (C) :
- $\text{KO}_2$

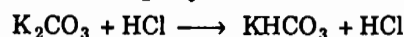
$\text{KO}_2$  is paramagnetic (with one unpaired electron in  $\text{O}_2^-$ ) while  $\text{K}_2\text{O}$  and  $\text{K}_2\text{O}_2$  are diamagnetic.

- 28.
- $\text{K}_2\text{CO}_3$

- 29.
- $\text{Li}_2\text{CO}_3$
- : 25%
- $\text{K}_2\text{CO}_3$
- : 75% (
- $\text{CO}_2$
- is due to
- $\text{Li}_2\text{CO}_3$
- only)



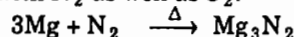
30. Methyl orange; phenolphthalein ceases to indicate colour change after 50% of
- $\text{K}_2\text{CO}_3$
- has reacted with acid.



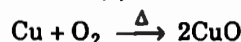
31. (A) :
- $\text{K}_2\text{SO}_4$
- (B) :
- $\text{BaSO}_4$
- (C) :
- $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

- 32.
- $17.4 \text{ g L}^{-1}$

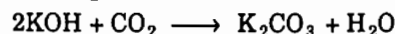
33. (a) Mg reacts with
- $\text{N}_2$
- as well as
- $\text{O}_2$
- .



- (b)
- $\text{O}_2$
- if left unreacted in (a) reacts with Cu



- (c) KOH absorbs
- $\text{CO}_2$



34. (A) :
- $\text{Li}_3\text{N}$
- (B) :
- $\text{LiOH}$
- (C) :
- $\text{NH}_3$
- (D) :
- $\text{Li}$
- (E) :
- $\text{N}_2$

35. (a) Li forms
- $\text{Li}_2\text{C}_2$
- , Na does not form carbide with carbon

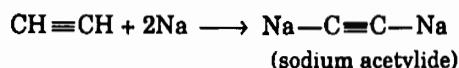
- (b)
- $[\text{Li}(\text{NH}_3)_4]^+$
- exists, Na does not form

- (c)
- $\text{Li}_2\text{CO}_3$
- ,
- $\text{Li}_3\text{PO}_4$
- ,
- $\text{LiF}$
- are insoluble while sodium salts are soluble

- (d)
- $\text{LiCl}$
- is covalent while
- $\text{NaCl}$
- is ionic

- (e)
- $\text{NaHCO}_3$
- is stable in solid and aqueous solution while
- $\text{LiHCO}_3$
- exists in aqueous solution but solid
- $\text{LiHCO}_3$
- does not exist.

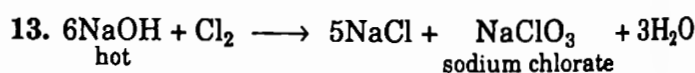
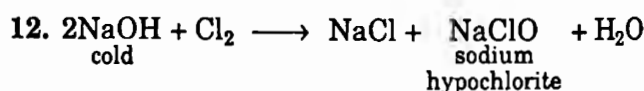
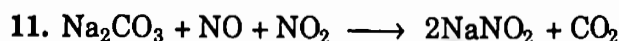
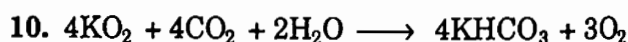
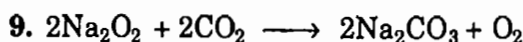
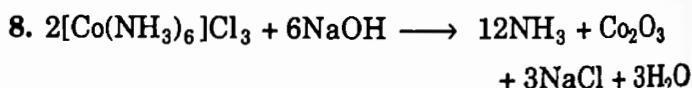
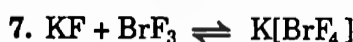
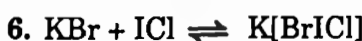
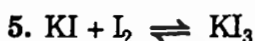
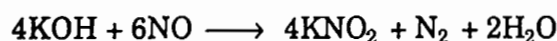
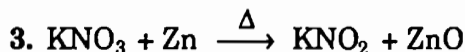
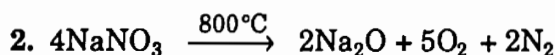
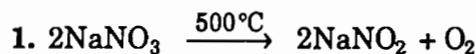
36. Sodium acetylide (
- $\text{Na}_2\text{C}_2$
- ) is formed when sodium reacts with acetylene

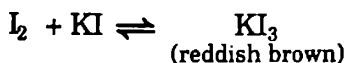
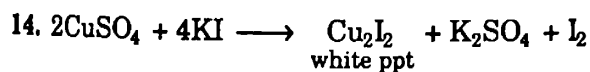


37. (i)
- $\text{Li}_2\text{O}$
- (ii)
- $\text{Na}_2\text{CO}_3$

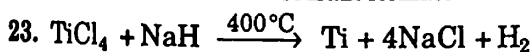
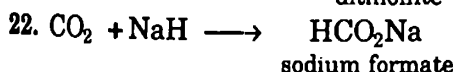
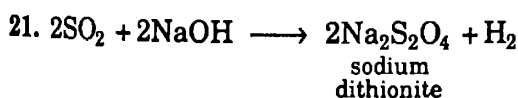
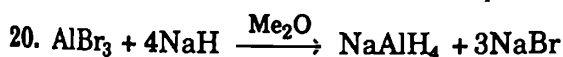
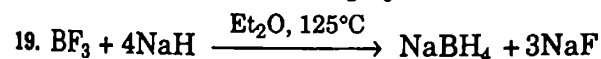
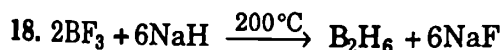
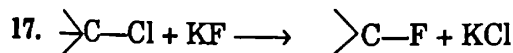
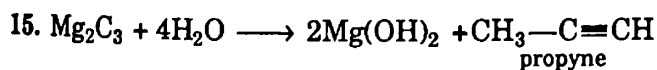
## Additional Reactions and Facts of Alkali Metals IA

### Reactions :





More reactions of KI are given in halogen family of *p*-block elements.



### Important Facts of Alkali Metals

- Francium is radioactive; its longest-lived isotope  $^{223}\text{Fr}$  has a half-life of only 21 min.
- Li and Mg, show diagonal relationship.
- Among the alkali metal K, Rb and Cs form superoxides  $\text{MO}_2$ ;  $\text{O}_2^-$  is paramagnetic.
- Increasing stability of the peroxide or superoxide, as the size of the metal ion increases is due to the stabilisation of large anions by larger cation through lattice energy effects.

- Li forms  $\text{Li}_3\text{N}$  (nitrides).
- $\text{Li}^+$  being of smallest size has the highest hydration enthalpy which accounts for its high negative  $E^\circ$  value and its reducing power.
- Alkali metals dissolve in liquid  $\text{NH}_3$ ; solutions are coloured due to solvated electrons. In dilute solution, ammoniated solution is paramagnetic but in concentrated solution, unpaired electrons get paired and it becomes diamagnetic.
- $\text{NaOH} \cdot n\text{H}_2\text{O}$  ( $n = 1, 2, 3, 4, 5$  and  $7$ ) has been prepared.
- $\text{LiX}$  have partial covalent character due to smaller size of cation.
- Carbonates and in most cases bicarbonates also (except that of Li) are highly stable to heat. Along a group, stability increases.  $\text{LiHCO}_3$  does not exist in solid state.
- $\text{LiCl}$  is deliquescent and crystallises as a hydrate  $\text{LiCl} \cdot 2\text{H}_2\text{O}$ .
- $\text{KO}_2$  is  $\text{CO}_2$  and  $\text{CO}$  absorber, and  $\text{O}_2$  emitter. This finds application in submarines, space capsules and breathing masks.
- $\text{NaOH}$  is prepared from electrolysis of aqueous  $\text{NaCl}$  solution using
  - Castner Kellner cell
  - Diaphragm cell
  - Nafion membrane cell
- $\text{Na}_2\text{CO}_3$  is prepared by Solvay process.
- Alkali metals impart colour in flame.
- $\text{KNO}_3$  has been used for centuries as the oxidising agent in gun powder. A mixture of  $\text{KNO}_3$ , charcoal and sulphur will spontaneously react when ignited.
- $\text{Li}_2\text{CO}_3$  has been used for than 40 yr as a treatment for bipolar disorder.



# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** On the basis of the following values of hydration energies and lattice energies, calculate heat of solution of LiCl, NaCl and KCl.

| Hydration energy<br>$\Delta H_{\text{hydr.}}$ (kJ mol <sup>-1</sup> ) |      | Lattice energy<br>$\Delta H_{\text{U}}$ (kJ mol <sup>-1</sup> ) |      |
|-----------------------------------------------------------------------|------|-----------------------------------------------------------------|------|
| Li <sup>+</sup>                                                       | -499 | LiCl                                                            | -840 |
| Na <sup>+</sup>                                                       | -390 | NaCl                                                            | -776 |
| K <sup>+</sup>                                                        | -305 | KCl                                                             | -703 |
| Cl <sup>-</sup>                                                       | -382 |                                                                 |      |

**Solution**  $\Delta H_{\text{solution}} = \Delta H_{\text{hydr.}} - \Delta H_{\text{U}}$

A solute  $M^+X^-$  dissolves in water if  $\Delta H_{\text{solution}}$  (heat of solution) is positive.

$$\Delta H_{\text{hydr.}} : \text{LiCl} = -499 - 382 = -881 \text{ kJ mol}^{-1}$$

$$\text{NaCl} = -390 - 382 = -772 \text{ kJ mol}^{-1}$$

$$\text{KCl} = -305 - 382 = -687 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{sol.}} : \text{LiCl} = -881 - (-840) = -41 \text{ kJ mol}^{-1}$$

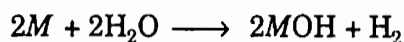
$$\text{NaCl} = -772 - (-776) = +4 \text{ kJ mol}^{-1}$$

$$\text{KCl} = -687 - (-703) = +16 \text{ kJ mol}^{-1}$$

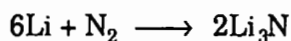
**Problem 2.** Which of the following methods would you use to extinguish a fire of lithium, sodium or potassium metals? Explain why some of these are unsuitable, and give the reaction involved?

- (a) Water (b) Nitrogen (c) Carbon dioxide  
(d) Asbestos blanket

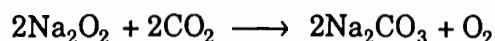
**Solution** (a) Water can't be used since metal catches fire forming hydroxide and hydrogen.



- (b) Nitrogen forms nitride with Li.

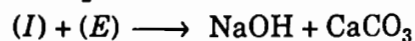
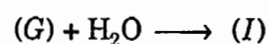
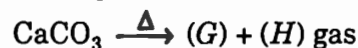
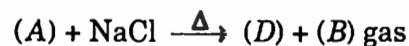
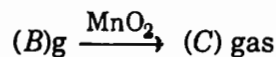
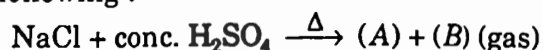


- (c) If metal has converted to oxide or peroxide, CO<sub>2</sub> may react producing O<sub>2</sub> that would further worsen the situation.

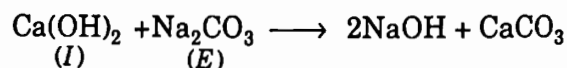
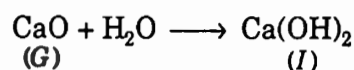
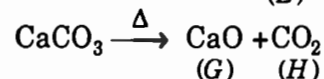
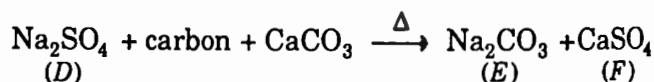
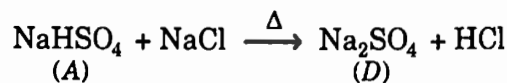
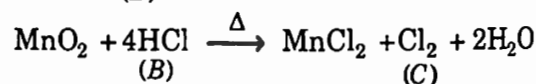
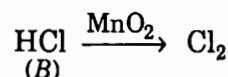


- (d) Asbestos blanket is best suited.

**Problem 3.** NaCl in earlier days used to manufacture NaOH and Cl<sub>2</sub> involving following steps. Identify (A) to (I) in the following :

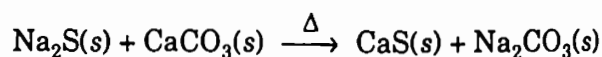
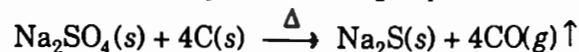
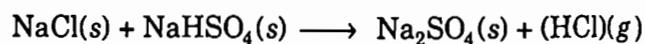
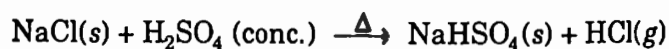


**Solution**  $\text{NaCl} + \text{conc. } H_2SO_4 \longrightarrow \underset{(A)}{\text{NaHSO}_4} + \underset{(B)}{\text{HCl}}$



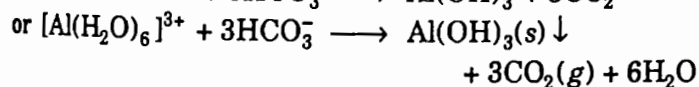
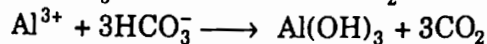
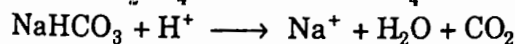
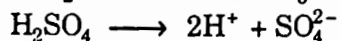
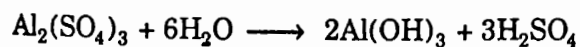
**Problem 4.** Propose a method of synthesising Na<sub>2</sub>CO<sub>3</sub> from NaCl.

**Solution**



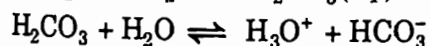
**Problem 5.** In some foam-type fire extinguishers the reactants are Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (aq) and NaHCO<sub>3</sub> (aq). When the extinguisher is activated, these reactants are allowed to mix producing Al(OH)<sub>3</sub> (s) and CO<sub>2</sub> (g). The Al(OH)<sub>3</sub> - CO<sub>2</sub> foam extinguishes the fire. Write net ionic equation to represent this reaction.

**Solution**  $\text{Al}_2(\text{SO}_4)_3$  solution is acidic due to hydrolysis.

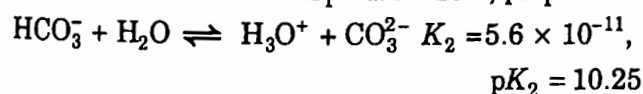


**Problem 6.** Mention various factors involved in the control of the pH of blood.

**Solution** Several factors are involved in the control of the pH of blood. A particularly important one is the ratio of dissolved  $\text{HCO}_3^-$  (from  $\text{NaHCO}_3$ ) to  $\text{H}_2\text{CO}_3$  (aq.  $\text{CO}_2$ ,  $\text{CO}_2 + \text{H}_2\text{O}$ ).  $\text{CO}_2$  is soluble in water and in aqueous solution it reacts to a limited extent to produce  $\text{H}_2\text{CO}_3$ .



$$K_1 = 4.2 \times 10^{-7}, \text{p}K_1 = 6.38$$



$$\text{p}K_2 = 10.25$$

Since  $K_2 \ll K_1$ , hence  $K_1$  is of importance and involved in the buffer. Then

$$\text{pH} = \text{p}K_1 + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

Generally  $\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 10 : 1$  so that  $\text{pH}(\text{blood}) = 7.4$

If lactic acid is produced due to exercise,  $\text{HCO}_3^-$  can be converted to  $\text{H}_2\text{CO}_3$ , but due to large ratio of  $[\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$ , pH remains almost constant.

To control alkalinity, extra  $\text{H}_2\text{CO}_3$  is required.  $\text{CO}_2$  (in the lungs) can be absorbed to keep  $\text{H}_2\text{CO}_3$  in the blood constant and thus its pH.

**Problem 7.** Explain the following:

- Why should an alkali never be put into a burette?
- Large quantities of rock salt are used on roads in winter (in cold countries).
- Why is it that lithium salts have a greater degree of covalent character than other halides of the group?
- Why is it that although  $\text{Li}^+$  is far smaller than the other metal ions, it moves through a solution less rapidly than the others?
- $\text{LiF}$  has the lowest solubility of the group 1 metal halides.

**Solution** (a) It gives a deposit of a carbonate with  $\text{CO}_2$  in the air, which can jam the tap.

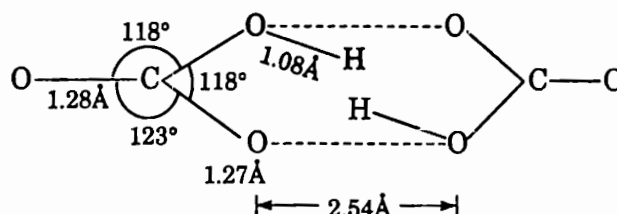
- They lower the freezing point of water, thus preventing ice formation.
- The small size of  $\text{Li}^+$  gives it a large polarising power hence covalent nature of its compounds increases. It can be viewed in terms of Fajan's rule:

- smaller the cation
  - larger the anion
  - greater the charge
  - thus greater the polarising power
- hence, greater the covalent nature.

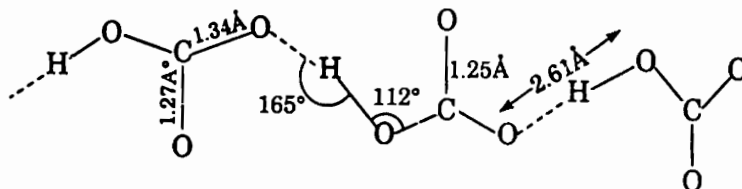
- Smaller the size of cation, larger the charge (hence, greater the charge density) then greater the hydration. The dense charge of  $\text{Li}^+$  attracts several layers of water molecules around it. They increase the effective size of the ion, thus slowing it down.
- The small size of both the  $\text{Li}^+$  and  $\text{F}^-$  ions leads to a very large lattice energy hence solubility is least.

**Problem 8.** Give the distinct features of structures of sodium and potassium bicarbonates.

**Solution** The structures of sodium and potassium bicarbonates provide interesting examples of hydrogen bonding. The potassium salt contains a dimeric anion as shown in the following structure.

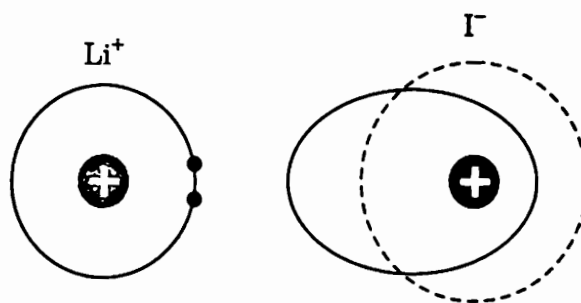


In the sodium bicarbonate, the  $\text{HCO}_3^-$  anions form an infinite chain



**Problem 9.** Lithium compounds have covalent character. Explain.

**Solution** High polarising power of  $\text{Li}^+$  ion due to its smaller size makes lithium compounds (particularly



Polarisation of electron charge cloud of iodide by lithium ion

lithium halides) predominantly covalent. If  $\text{Li}^+\text{I}^-$  is considered fully ionic compound, its dipole moment in the gaseous state would be 11.5 debye (D) but its experimental value comes out to be 3.25 D. This is due to distortion of electron charge cloud of the iodide ion by the lithium ion, which results in decrease in ionic character (hence the decrease in dipole moment) and increase in covalent character of  $\text{LiI}$ .

## Explanation

(a) **LiF is much less soluble than LiCl, but AgF is much more soluble than AgCl.**

- LiF has such a high lattice energy (U) that the high solvation energy of  $F^-$  is not sufficient to make it more soluble than LiCl. The difference in U is not so great for AgF and AgCl and the high solvation energy of  $F^-$  determines relative solubilities.

(b) **Lithium salts are not involved in alums.**

- In alums,  $M_2SO_4 \cdot M_2(SO_4)_3 \cdot 24H_2O$

( $M^I$  = alkali metal,  $M^{III}$  = a trivalent metal), each alkali metal is coordinated to six separate water molecules :

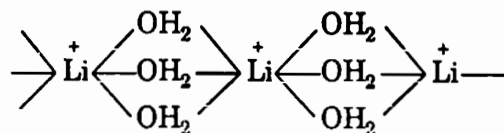


Lithium does not form alums, probably because the small  $[Li(H_2O)_6]^+$  is too small to form stable lattice required for alum formation.

(c) **In lithium salts, lithium is surrounded octahedrally by six water molecules.**

- Due to smallest size,  $Li^+$  ion is hydrated to maximum and it is surrounded octahedrally by six water .

Molecules — the octahedral share faces, forming chains.



(d) **Solubility of iodides of alkali metals in water is in codes**



**But that of fluorides is in reverse order**



- $LiI > NaI > KI > RbI > CsI$  (solubility)

$$\text{Lattice energy} \propto \frac{1}{r_+ + r_-}$$

Since,  $r_- > r_+$ , the sum will not change too much as  $r_+$  increases. As a result the lattice energy will not change significantly as  $r_+$  increases. Thus decrease in lattice energy is not as fast as decrease in hydration energy. Thus, more decrease in hydration energy results in decrease in solubility. Thus, solubility decreases as



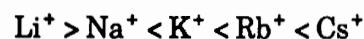
With a small anion as ( $F^-$ ), the lattice energy decreases more rapidly along a series of salts with increasing cation size and thus solubility increases.



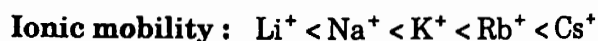
(e) **Ionic mobility of alkali metals ion is in order**



- Size of alkali metal ions is in order



Smaller the size, larger the hydration. Thus,  $Li^+$  is most hydrated and  $Cs^+$  is least hydrated. Hydration results in decrease in ionic mobility. Thus,  $Li^+$  has least ionic mobility and  $Cs^+$  maximum, order being:



(f) **On being heated in excess supply of air, K, Rb and Cs form superoxide rather than oxides and peroxides.**

- As a general rule, to the large cations stabilise larger anions.  $K^+$ ,  $Rb^+$  and  $Cs^+$  are larger cations and  $O_2^-$  (superoxide) is also larger anion. Thus, when  $MO_2$  is formed, it is stabilised, hence its formation is preferred to oxides and peroxides (which are relatively smaller ions).

# Master Exercises

## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

1. Name the bicarbonate of alkali metal which does not exist in solid state?
2. Name the binary salt of potassium which shows paramagnetic character and which is used in life-saving devices?
3. Compare the following :
  - (a)  $\text{Li}^+$  and  $\text{Be}^{2+}$  in ionic conductance
  - (b)  $\text{Li}^+$  and  $\text{K}^+$  in hydrated ionic size
  - (c)  $\text{LiCl}$  and  $\text{NaCl}$  in lattice energy
  - (d)  $\text{Na}_2\text{CO}_3$  and  $\text{Li}_2\text{CO}_3$  in thermal stability
  - (e)  $\text{Li}^+$  and  $\text{Na}^+$  in polarising power
  - (f)  $\text{LiI}$  and  $\text{CsI}$  in solubility in water.
4. Arrange  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{Al}^{3+}$ ,  $\text{N}^{3-}$  (each having 10 electrons) in increasing ionic radii.
5. Arrange  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{RbCl}$  and  $\text{CsCl}$  in increasing lattice energy.
6. Arrange  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  and  $\text{Rb}_2\text{CO}_3$  in increasing melting point.
7. Identify A to in the following sequence of reaction :
$$\text{Na} + \text{O}_2 \longrightarrow (\text{A}) \xrightarrow{\text{HCl}} (\text{B}) \xrightarrow[\text{ether}]{\text{H}^+/\text{K}_2\text{Cr}_2\text{O}_7} (\text{C})$$

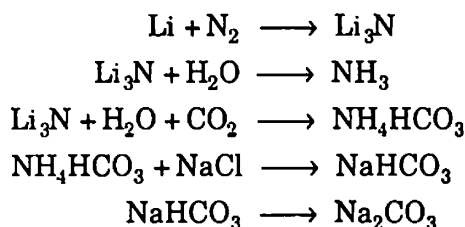
blue in  
ethereal layer
8. Arrange  $\text{LiClO}_4$ ,  $\text{NaClO}_4$ ,  $\text{KClO}_4$  and  $\text{RbClO}_4$  in increasing solubility.
9. Arrange fluorides of alkali metals in increasing solubility.
10. Potassium cobaltinitrite is used in qualitative analysis. Explain.
11.  $\text{Na}^+$  (cation) is smaller than  $\text{Na}$  (atom)
12. You have a mixture of  $\text{LiCl}$  and  $\text{NaCl}$ . Suggest a suitable solvent to separate the mixture.
13.  $\text{LiCl}$  has lower melting point than  $\text{NaCl}$ . Explain
14.  $\text{Li}_2\text{CO}_3$  decomposes into  $\text{CO}_2$  and  $\text{Li}_2\text{O}$  but other alkali carbonates are thermally stable. Explain.
15. What is oxone?
16. Why sodium is less reactive than potassium?
17.  $\text{Cs}$  metal is used in photoelectric cells,  $\text{Li}$  is not used. Explain.
18. Lithium is the only metal in alkali metals that forms nitride. Explain.
19. (a) What is formula of potassium superoxide?  
(b) What is oxidation state of potassium?  
(c) What is bond-order of superoxide ion?  
(d) What is magnetic moment of superoxide ion?
20. Aqueous  $\text{Na}_2\text{CO}_3$  is alkaline in nature. Explain
21. In the laboratory, you would have noticed that  $\text{NaOH}$  solution has some white deposit inside reagent bottle. Explain.
22. Pallets of  $\text{KOH}$  become wet when exposed to air. Explain.
23. Name the metal which floats on water without any apparent reaction with water.
24.  $\text{Li}$  resembles to element  $X$  which is not the member of alkali metals.
  - (a) Name  $X$
  - (b) What is group of  $X$ ?
  - (c) Mention two properties which resembles to that of  $\text{Li}$
25. Lithium on heating in air forms mainly  $\text{Li}_2\text{O}$  (oxide) and not peroxide ( $\text{Li}_2\text{O}_2$ ). Explain.
26. Give an example to verify that larger anion stabilise larger cation.
27. Name the salt of alkali metal that does not form double salts such as alums.
28. Baking soda or baking powder, they are different or same.

29.  $\text{KHCO}_3$  or  $\text{K}_2\text{CO}_3$  cannot be obtained Solvay process. Explain.
30. Give two oxidising properties given by  $\text{Na}_2\text{O}_2$ .

## Analytical Questions

1. The ionisation energies of group 1 elements (alkali metals) suggest that caesium should be most reactive but standard electrode potentials suggest that lithium is the most reactive. Reconcile these two observations.

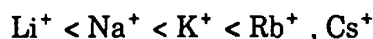
2. In the following sequence of reactions (unbalanced)



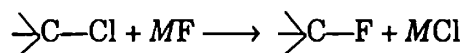
Calculate volume of  $\text{N}_2$  required at NTP to form 10.6 kg of  $\text{Na}_2\text{CO}_3$ .

3. Comment on each of the following observations:

- (a) The mobilities of the alkali metal ions in aqueous solutions are:



- (b) Lithium is the only alkali metal to form a stable nitride.
- (c) The solubility of sodium sulphate in water increases up to  $32^\circ\text{C}$  and thereafter decreases.
- (d)  $E^\circ$  for  $M^+(aq) + e^- \rightleftharpoons M(s)$  is nearly constant for the alkali metals.
- (e) For the replacement of chlorine in organic compounds by fluorine by the autoclave reaction



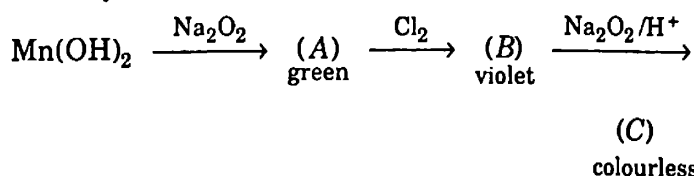
KF is a better reagent than NaF.

4. One mole each of  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CH}\equiv\text{CH}$  is treated with excess of Na metal.
- (a) Write reactions
- (b) In which case, yield of  $\text{H}_2$  is better (in terms of volume of  $\text{H}_2$  at STP)
- (c) Compare % yield ( $\text{H}_2$ ) in terms of mass of reactant.

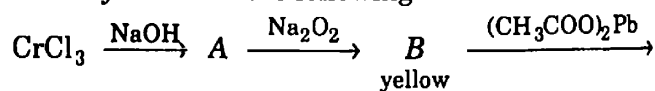
5. Explain polarisation by  $\text{Li}^+$  ion.

6. Na and K are strong reducing agents. Give examples.

7. Identify A to C in the following :



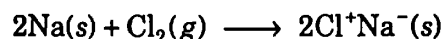
8. Identify A to C in the following



C  
yellow precipitate

9. (a) A white solid is either  $\text{Na}_2\text{O}$  or  $\text{Na}_2\text{O}_2$ . A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid. Identify the substance and explain with balanced equation.
- (b) Explain what would happen to red litmus if the white solid were the other compound?
10. (A) is binary salt of alkali metal. 0.71 g of A on heating with excess of sulphur forms (B) and which in aqueous solution gives 2.33 g white precipitate (insoluble in conc. HCl) with aqueous  $\text{BaCl}_2$  solution. A crystalline double salt (C) formed from  $\text{Al}_2(\text{SO}_4)_3$  and (B) ( $\text{Ba} = 137$ ,  $\text{Al} = 27$ ,  $\text{S} = 32$ )
- (a) What is A? (b) What is B?
- (c) What is C? (d) What is amount of C?

11. Calculate the energy change for the alternating reaction that yields chlorine sodium ( $\text{Cl}^+\text{Na}^-$ ) and then explain that why sodium chloride is prepared



Lattice energy of  $\text{Cl}^+\text{Na}^- = -787 \text{ kJ mol}^{-1}$

Electron affinity of Na =  $-52.9 \text{ kJ mol}^{-1}$

Ionisation energy of Cl =  $+1251 \text{ kJ mol}^{-1}$

BE of  $\text{Cl}_2 = 244 \text{ kJ mol}^{-1}$

Heat of sublimation of Na(s) =  $107.3 \text{ kJ mol}^{-1}$

$\Delta H_f(\text{NaCl}) = -411 \text{ kJ mol}^{-1}$

Also make Born-Haber cycle for  $\text{Cl}^+\text{Na}^-(\text{s})$

## NCERT Problems

1. The alkali metals follow the noble gases in their atomic structure. What properties of these metals can be predicted from this information?
2. What happens when
- sodium metal is dropped in water?
  - sodium metal is heated in free supply of air?
  - sodium peroxide dissolves in water?
3. Name the alkali metals which form superoxides when heated in excess of air.
4. Name the metal which floats on water without any apparent reaction with it.
5. List three properties of lithium in which it differs from the rest of the alkali metals.
6. Name the chief factor responsible for the anomalous behaviour of lithium.

- When an alkali metal dissolves in liquid ammonia the solution acquires different colours. Explain the reasons for this type of colour change.
- What is meant by 'diagonal relationship' in the Periodic Table? What is it due to?
- Describe in detail the manufacture of sodium carbonate by the Solvay process. State the principles involved in this process.
- Describe three industrial uses of caustic soda. Describe one method of manufacture of sodium hydroxide. What happens when sodium hydroxide reacts with (i) aluminium metal (ii)  $\text{CO}_2$  (iii)  $\text{SiO}_2$ ?
- Why is that the s-block elements never occur free in nature? What are their usual modes of occurrence and how are they generally prepared?
- Compare the solubility and thermal stability of the following compounds of the alkali metals with those of the alkaline earth metals
  - nitrates
  - carbonates
  - sulphates
- Explain what happens when
  - sodium hydrogen carbonate is heated?
  - sodium amalgam reacts with water?
  - fused sodium metal reacts with ammonia?
- Mention the general trends in Group 1 and in Group 2 with increasing atomic number with respect to
  - density
  - melting point
  - atomic size
  - ionization enthalpy
- Starting with sodium chloride how would you proceed to prepare (state the steps only)?
  - Sodium metal
  - Sodium hydroxide
  - Sodium peroxide
  - Sodium carbonate
- State as to why
  - lithium on being heated in air mainly forms the monoxide and not the peroxide?
  - an aqueous solution of sodium carbonate gives alkaline tests?
  - sodium is prepared by electrolytic method and not by chemical method?
- How do the following properties change on moving from group 1 to group 2 in the Periodic Table?
  - Atomic size
  - Ionisation enthalpy
  - Density
  - Melting points
- Like lithium in group 1, beryllium shows anomalous behaviour in group 2. Write three such properties of beryllium which make it anomalous in the group.
- Comment on each of the following observations :
  - The mobilities of the alkali metal ions in aqueous solution are  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$
  - Lithium is the only alkali metal to form a nitride directly
  - $E^\circ$  for  $M^{2+}(\text{aq}) + 2e^- \longrightarrow M(\text{s})$  (where  $M = \text{Ca}, \text{Sr}$  or  $\text{Ba}$ ) is nearly constant
  - $\text{LiF}$  is least soluble among the fluorides of alkali metals
- Why does the following reaction
 
$$\text{>C-Cl} + \text{MF} \longrightarrow \text{>C-F} + \text{MCl}$$
 proceed better with  $\text{KF}$  with than  $\text{NaF}$ ?
- Compare and contrast the chemistry of group 1 metals with that of group 2 metals with respect to
  - nature of oxides
  - solubility and thermal stability of carbonates
  - polarizing power of cations
  - reactivity and reducing power
- Describe two important uses of each of the following.
  - caustic soda
  - sodium carbonate
  - quicklime
- State as to why
  - A solution of  $\text{Na}_2\text{CO}_3$  is alkaline?
  - Alkali metals are prepared by electrolysis of their fused chlorides?
  - Sodium is found more useful than potassium?
- Write balanced equations for reactions between
  - $\text{Na}_2\text{O}_2$  and water
  - $\text{KO}_2$  and water
  - $\text{Na}_2\text{O}$  and  $\text{CO}_2$

## Exercise 2

### (Stage 2 : High Skill Problem Solving)

#### Only One Option Correct

- Which is/are not correct configuration of s-block elements?
  - $(\text{Ar})3d^{10}4s^2$
  - $(\text{Ar})3d^{10}4s^1$
  - Both (a) and (b)
  - None of these

- Select correct statement(s).

- $\text{Li}_2\text{CO}_3$  decomposes into oxides while other alkali carbonates are thermally stable
- $\text{LiCl}$  is predominantly covalent
- $\text{Li}_3\text{N}$  is stable
- all of the above

3. Alkali metals resemble IB (copper family) in following respects  
 (a) +1 valency  
 (b) sulphates are water soluble  
 (c) oxides are strong base  
 (d) oxides are strong acids
4. Select incorrect statement.  
 (a)  $\text{Na}_2\text{CO}_3$  is thermally stable while  $\text{Ag}_2\text{CO}_3$  decomposes into Ag,  $\text{CO}_2$  and  $\text{O}_2$   
 (b)  $\text{Ag}^+$  forms complexes,  $\text{Na}^+$  does not  
 (c)  $\text{NaCl}$  is water soluble,  $\text{AgCl}$  is insoluble  
 (d)  $\text{NaCl}$  and  $\text{AgCl}$  both give colour in flame when ignited
5. A colourless solid (X) on heating evolved  $\text{CO}_2$  and also gave a white residue, soluble in water. Residue also gave  $\text{CO}_2$  when treated with dilute acid. (X) is  
 (a)  $\text{Na}_2\text{CO}_3$  (b)  $\text{CaCO}_3$   
 (c)  $\text{Ca}(\text{HCO}_3)_2$  (d)  $\text{NaHCO}_3$
6. Which of the following is preferentially formed on reaction of oxygen and potassium?  
 (a)  $\text{K}_2\text{O}_2$  (b)  $\text{KO}_2$   
 (c)  $\text{K}_2\text{O}$  (d)  $\text{K}_2\text{O}_3$
7.  $\text{CO}_2$  gas along with solid (Y) is obtained when sodium salt (X) is heated. (X) is again obtained when  $\text{CO}_2$  gas is passed into aqueous solution (Y). (X) and (Y) are  
 (a)  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{O}$  (b)  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$   
 (c)  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$  (d)  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$
8. Which salt can be used to identify coloured cation?  
 (a) Borax (b) Microcosmic salt  
 (c) Both (a) and (b) (d) None of these
9. Intermediate formed by heating microcosmic salt and which forms coloured bead with coloured cation is  
 (a)  $\text{NH}_3$  (b)  $\text{H}_3\text{PO}_3$   
 (c)  $\text{NaPO}_3$  (d)  $\text{H}_2\text{O}$
10. Molten sodium chloride conducts electricity due to the presence of  
 (a) free electrons (b) ions  
 (c) Na atom (d) Cl atom
11. Which is the major constituent of gun powder?  
 (a) Nitre (b) Sulphur  
 (c) Charcoal (d) Chile salt petre
12. When  $\text{SO}_2$  gas is passed into aqueous  $\text{Na}_2\text{CO}_3$ , product formed is  
 (a)  $\text{NaHSO}_4$  (b)  $\text{Na}_2\text{SO}_4$   
 (c)  $\text{NaHSO}_3$  (d)  $\text{Na}_2\text{SO}_3$
13.  $\text{CO}_2$  cannot be obtained by heating  
 (a)  $\text{Na}_2\text{CO}_3$  (b)  $\text{CaCO}_3$   
 (c)  $\text{Li}_2\text{CO}_3$  (d)  $\text{Ca}(\text{HCO}_3)_2$
14. Some of alkali metal salts are coloured.  $\text{Na}_2\text{CrO}_4$ —yellow,  $\text{KMnO}_4$ —pink,  $\text{K}_2\text{MnO}_4$ —green. It is due to  
 (a) cations are coloured ions  
 (b) anions are coloured ions  
 (c) both (a) & (b) are correct  
 (d) None of the above is correct
15. Na and Li are placed in dry air. We get  
 (a)  $\text{NaOH}$ ,  $\text{Na}_2\text{O}$ ,  $\text{Li}_2\text{O}$   
 (b)  $\text{Na}_2\text{O}$ ,  $\text{Li}_2\text{O}$   
 (c)  $\text{Na}_2\text{O}$ ,  $\text{Li}_2\text{O}$ ,  $\text{Li}_3\text{N}$ ,  $\text{NH}_3$   
 (d)  $\text{Na}_2\text{O}$ ,  $\text{Li}_3\text{N}$ ,  $\text{Li}_2\text{O}$
16. All alkali metals form following compound except  
 (a) amide,  $\text{MNH}_2$   
 (b) superoxide like  $\text{KO}_2$   
 (c) ionic 'salt-like' hydride  $\text{MH}$   
 (d) basic oxides
17. Match the compounds (given in X) with their colours (given in Y)
- | X                                        | Y                 |
|------------------------------------------|-------------------|
| A. $\text{Li}_3\text{N}$                 | I Pale yellow     |
| B. $\text{K}_2\text{O}$                  | II Orange         |
| C. $\text{Cs}_2\text{O}$ , $\text{KO}_2$ | III Bright yellow |
| D. $\text{Rb}_2\text{O}$                 | IV Ruby red       |
- 
- | A      | B  | C   | D   | A                 | B   | C | D  |
|--------|----|-----|-----|-------------------|-----|---|----|
| (a) IV | I  | II  | III | (b) II            | III | I | IV |
| (c) I  | II | III | IV  | (d) None of these |     |   |    |
18. Which of the following is best  $\text{CO}_2$  absorber as well as source of  $\text{O}_2$  in submarines?  
 (a)  $\text{KO}_2$  (b)  $\text{NaOH}$   
 (c)  $\text{KOH}$  (d)  $\text{LiOH}$
19. Following are the ionisation potential values of ( $I_1$ ) 899  $\text{kJ mol}^{-1}$ , ( $I_2$ ) 1757  $\text{kJ mol}^{-1}$ , ( $I_3$ ) 15000  $\text{kJ mol}^{-1}$   
 (a) Na (b) K  
 (c) Be (d) Ne
20. A compound which can be used in space vehicles both to absorb  $\text{CO}_2$  and liberate  $\text{O}_2$  is  
 (a)  $\text{NaOH}$  (b)  $\text{Na}_2\text{O}$   
 (c)  $\text{Na}_2\text{O}_2$  (d)  $\text{CaO} + \text{NaOH}$
21. Which of the following changes is not realised in the laboratory?  
 (a) Absorption of  $\text{NO}$  by alkaline sodium sulphite to form a compound  
 (b) Combustion of metallic Mg in  $\text{CO}_2$   
 (c) Heating hydrated magnesium chloride to get the anhydrous salt  
 (d) 'Displacement' of chlorine from  $\text{KClO}_3$  by iodine to form  $\text{KIO}_3$
22. Which is not s-block element?  
 (a)  $[\text{Ar}] 4s^2 3d^{10} 4p^6 5s^1$  (b)  $1s^2 2s^2 2p^1$   
 (c)  $1s^2 2s^1 2p^1$  (d)  $[\text{Ar}] 4s^1 4p^1$

23. Which will give  $N_2O$  on heating?  
 (a)  $NH_4NO_2$  (b)  $NH_4NO_3$   
 (c)  $NaNO_3$  (d)  $LiNO_3$
24. Nitrate can be converted into metal oxide on heating in case of  
 (a) Li (b) Na  
 (c) both (a) and (b) (d) None of these
25. Automobile grease is obtained from  
 (a)  $CH_3COONa$  (b)  $C_{17}H_{35}COONa$   
 (c)  $CH_3CH_2COOLi$  (d)  $C_{17}H_{35}COOLi$
26.  $Li_2CO_3$  is  
 (a) added to bauxite in the electrolytic production of aluminium  
 (b) used to toughen glass  
 (c) used as medicine as it affects the balance between  $Na^+$  and  $K^+$ , and  $Mg^{2+}$  and  $Ca^{2+}$   
 (d) all of the above are correct
27. Which cannot be used to generate  $H_2$ ?  
 (a)  $Al + NaOH$  (b)  $Zn + NaOH$   
 (c)  $Mg + NaOH$  (d)  $LiH + H_2O$
28. There is loss in weight when mixture of  $Li_2CO_3$  and  $Na_2CO_3 \cdot 10H_2O$  is heated strongly. This loss is due to  
 (a)  $Li_2CO_3$  (b)  $Na_2CO_3 \cdot 10H_2O$   
 (c) both (a) and (b) (d) None of these
29. Which disproportionates into  $M_2O_2$  (peroxide) and  $M$  (metal) on heating?  
 (a)  $Li_2O$  (b)  $Na_2O$   
 (c) Both (a) and (b) (d) None of these
30. Reagent used as fixer in photography  
 (a)  $AgBr$  (b)  $AgNO_3$   
 (c)  $Na_2S_2O_3 \cdot 5H_2O$  (d) both (a) and (c)
31. Which can dissolve  $I_2$ ?  
 (a) KI (b) NaI  
 (c) Both (a) and (b) (d) None of these
32. The deep colour produced when iodine is dissolved in a solution of potassium iodide is caused by the presence of  
 (a)  $I_2$  (b)  $I^-$   
 (c)  $I_3^-$  (d)  $I_2^-$
33. Alkali metals dissolve in liquid  $NH_3$ , then which of the following observation are true?  
 (a)  $H_2$  gas is liberated  
 (b) Solution is blue due to the presence of solvated electrons  
 (c) Solution is conducting  
 (d) All of the above are correct
34. Which is incorrect statement?  
 (a) The heats of hydration of the dipositive alkaline earth metal ions decrease with an increase in their ionic size.  
 (b)  $NaNO_3$  forms  $Na_2O$  on heating  
 (c) Hydration of alkali metal ion is less than that of II A.  
 (d) Alkaline earth metal ions, because of their much larger charge to size ratio, exert a much stronger electrostatic attraction on the oxygen of water molecule surrounding them.
35.  $NaOH$  is not used in  
 (a) paper industry (b) soap industry  
 (c) rayon industry (d) plastic industry
36. Match compounds given in (X) with their uses in (Y)
- | X             | Y                   |
|---------------|---------------------|
| A. $Na_2CO_3$ | I glass             |
| B. $Na_2SO_3$ | II bleach           |
| C. $NaOH$     | III $SO_2$ absorber |
| D. $NaOCl$    | IV detergent        |
- hence, correct order is
- | A      | B  | C   | D   | A       | B   | C  | D  |
|--------|----|-----|-----|---------|-----|----|----|
| (a) IV | I  | III | II  | (b) I   | III | IV | II |
| (c) II | IV | I   | III | (d) III | II  | IV | I  |
37. Match the compounds/metal in (X) with their uses in (Y).
- | X                       | Y                                |
|-------------------------|----------------------------------|
| A. Liquid sodium metal  | I. Breathing apparatus submarine |
| B. Potassium stearate   | II. Explosive                    |
| C. Potassium nitrate    | III. Coolant in nuclear reaction |
| D. Potassium superoxide | IV. Soft soap                    |
- hence correct order is
- | A      | B   | C   | D  | A       | B  | C   | D |
|--------|-----|-----|----|---------|----|-----|---|
| (a) I  | III | II  | IV | (b) III | IV | II  | I |
| (c) II | I   | III | IV | (d) IV  | II | III | I |
38. Lattice energy (numerical value) of chloride of alkali metals is in order  
 (a)  $LiCl > NaCl > KCl > RbCl > CsCl$   
 (b)  $LiCl < NaCl < KCl < RbCl < CsCl$   
 (c)  $NaCl < KCl < LiCl < RbCl < CsCl$   
 (d)  $NaCl < KCl < RbCl < CsCl < LiCl$
39. Which is most stable halide of alkali metal?  
 (a) Sodium fluoride (b) Sodium bromide  
 (c) Sodium chloride (d) Sodium iodide
40. Which is a pair of paramagnetic species?  
 (a)  $KO_2, NO_2$  (b)  $K_2O_2, KO_2$   
 (c)  $K_2O, NO_2$  (d)  $NO_2, N_2O_2$
41. Baking powder contains  
 (a)  $NaHCO_3, Ca(H_2PO_4)_2$  and starch  
 (b)  $NaHCO_3, Ca(H_2PO_4)_2$   
 (c)  $NaHCO_3$ , starch  
 (d)  $NaHCO_3$
42. Which does not exist in solid state?  
 (a)  $NaHCO_3$  (b)  $NaHSO_3$   
 (c)  $LiHCO_3$  (d)  $CaCO_3$



43. Following compounds are used in fire-works

- (a)  $\text{LiNO}_3$  (b)  $\text{BaCl}_2$   
(c)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (d) all of these

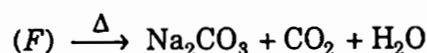
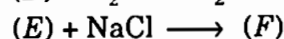
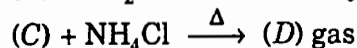
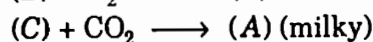
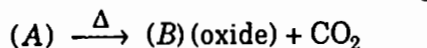
44. When NO is passed into KOH solution, products are

- (a)  $\text{N}_2$  (b)  $\text{N}_2\text{O}$   
(c) both (a) and (b) (d) None of these

45. Which has least molar solubility in  $\text{H}_2\text{O}$ ?

- (a)  $\text{LiCl}$  (b)  $\text{NaCl}$   
(c)  $\text{KCl}$  (d)  $\text{CsCl}$

Q. 46 to 49 are based on following reactions:



46. Name of the process is

- (a) Solvay (b) ammonia-soda  
(c) both (a) & (b) correct (d) None is correct

47. (A) is

- (a)  $\text{Ca}(\text{HCO}_3)_2$  (b)  $\text{CaCO}_3$   
(c)  $\text{CaO}$  (d)  $\text{Na}_2\text{CO}_3$

48. (B) and (C) are

- (a)  $\text{CaO}$ ,  $\text{Ca}(\text{OH})_2$  (b)  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCO}_3$   
(c)  $\text{CaCO}_3$ ,  $\text{Ca}(\text{OH})_2$  (d)  $\text{Ca}(\text{OH})_2$ ,  $\text{CaO}$

49. (D), (E) and (F) are

- (a)  $\text{NH}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{HCO}_3$   
(b)  $\text{NH}_3$ ,  $\text{NH}_4\text{HCO}_3$ ,  $\text{NaHCO}_3$   
(c)  $\text{NH}_4\text{HCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$   
(d) None of the above

50. Out of  $\text{AgF}$ ,  $\text{CaF}_2$ ,  $\text{BeF}_2$ ,  $\text{MgF}_2$

- (a)  $\text{AgF}$  and  $\text{BeF}_2$  are soluble, and  $\text{CaF}_2$  and  $\text{MgF}_2$  are insoluble in water  
(b)  $\text{AgF}$  is soluble, others insoluble  
(c)  $\text{AgF}$  is insoluble, others are soluble  
(d) all are insoluble

51. To an acidified dichromate solution, a pinch of  $\text{Na}_2\text{O}_2$  and ether is added and shaken. What is observed?

- (a) Deep violet colour  
(b) Red colour changing to green  
(c) Copious evolution of oxygen  
(d) Bluish-green precipitate

52. Nitrolim is a

- (a) mixture of calcium carbide and nitrogen  
(b) mixture of calcium cyanamide and carbon  
(c) mixture of calcium cyanide and carbon  
(d) mixture of  $\text{NH}_4\text{CN}$  and  $\text{CaCN}$

53. The common name, "cream of tartar" refers to

- (a)  $\text{KHC}_4\text{H}_4\text{O}_6$   
(b)  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$   
(c)  $\text{KNaC}_4\text{H}_4\text{O}_6$   
(d)  $\text{Mg}_2(\text{OH})_2(\text{C}_4\text{H}_4\text{O}_6)\text{H}_2\text{O}$

54. Which of the following mixtures cannot be prepared?

- (a)  $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$   
(b)  $\text{Na}_2\text{CO}_3 + \text{NaOH}$   
(c)  $\text{NaHCO}_3 + \text{NaOH}$   
(d)  $\text{H}_2\text{CO}_3 + \text{NaHCO}_3$

55. Noble gases (like He, Ne, Ar, Kr etc.) are isolated from air. One of the steps is/are

- (a) heating air with Li or Mg  
(b) bubbling air into NaOH solution  
(c) both (a) and (b) are correct  
(d) None of the above is correct

56. Which is used to treat acid indigestion?

- (a)  $\text{Be}(\text{OH})_2$  (b)  $\text{KOH}$   
(c)  $\text{Mg}(\text{OH})_2$  (d)  $\text{Ca}(\text{OH})_2$

57. Which of the following is not used as food preservatives?

- (a)  $\text{NaCl}$  (b)  $\text{CH}_3\text{COOH}$   
(c)  $\text{C}_6\text{H}_5\text{COONa}$  (d)  $\text{HCHO}$

58. Which are involved in various physiological functions in animals?

- (a)  $\text{Na}^+$  (b)  $\text{K}^+$   
(c) Both (a) and (b) (d) None of these

59. Which is used in the treatment of manic-depressive disorders?

- (a)  $\text{Na}_2\text{CO}_3$  (b)  $\text{Li}_2\text{CO}_3$   
(c)  $\text{K}_2\text{CO}_3$  (d)  $\text{MgCO}_3$

60. Select correct statement(s).

- (a)  $\text{Li}_2\text{CO}_3$  is only sparingly soluble in water and no  $\text{LiHCO}_3$  has been isolated.  
(b)  $\text{K}_2\text{CO}_3$  cannot be made by a method similar to the ammonia-soda process.  
(c)  $\text{Li}_2\text{CO}_3$  and  $\text{MgCO}_3$  both are thermally stable.  
(d)  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$  is a mineral called trona.

61. Select correct statement(s).

- (a)  $\text{CaCO}_3$  is more soluble in a solution of  $\text{CO}_2$  than in  $\text{H}_2\text{O}$   
(b)  $\text{Na}_2\text{CO}_3$  is converted to  $\text{Na}_2\text{O}$  and  $\text{CO}_2$  on heating  
(c)  $\text{Li}_2\text{CO}_3$  is thermally stable  
(d) Presence of  $\text{CaCl}_2$  or  $\text{CaSO}_4$  in water causes temporary hardness

62. The alkalide ion is

- (a) diamagnetic (b) represented as  $\bar{\text{CH}}_3$   
(c) paramagnetic (d) represented as  $\bar{\text{CH}}_3^+$

63. Select correct statement(s).

- (a)  $\text{Mg}^{2+}$  ions are necessary for the activation of phosphate transfer enzymes.

- (b) Mg is present in chlorophyll used in photosynthesis in green plants.  
 (c) Operation of  $\text{Na}^+ - \text{K}^+$  pumps is biological.  
 (d) All the above are correct statements
64. The alkali metals dissolve in liquid  $\text{NH}_3$ , it is found that  
 (a) the dilute solutions are blue but the colour changes to bronze with increasing concentration  
 (b) the blue colour is due to the presence of solvated electrons  
 (c) the blue solutions are paramagnetic but the bronze-coloured solutions are diamagnetic  
 (d) all the facts given above are found
65. Select correct statement(s).  
 (a) Stability of peroxides and superoxides of alkali metals increases with increase in size of the metal ion  
 (b)  $\text{NaOH}$  does not form hydrated salt  
 (c) Increase in stability in (a) is due to stabilisation of large anions by larger cations through lattice energy effects  
 (d) The low solubility of  $\text{LiF}$  is due to its high lattice energy whereas low solubility of  $\text{CsI}$  is due to smaller hydration energy
66. Which one of the following is correct sequence followed by molar ionic conductance of the ions?  
 (a)  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+$   
 (b)  $\text{Rb}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$   
 (c)  $\text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Be}^{2+}$   
 (d)  $\text{Na}^+ < \text{K}^+ < \text{Li}^+ < \text{Rb}^+$
67. Which one among the following is the most soluble in water?  
 (a)  $\text{LiI}$  (b)  $\text{LiBr}$   
 (c)  $\text{LiCl}$  (d)  $\text{LiF}$
68. The stability of  $\text{K}_2\text{O}$ ,  $\text{K}_2\text{O}_2$  and  $\text{KO}_2$  is in order  $\text{K}_2\text{O} < \text{K}_2\text{O}_2 < \text{KO}_2$ . This increasing stability at the size of metal ion increases is due to stabilisation of  
 (a) larger cation by smaller anions through lattice energy effects  
 (b) larger cation by larger anions through lattice energy effects  
 (c) smaller cations by smaller anions through m.p.  
 (d) smaller cations by larger anions through m.p.
69.  $\text{M}_2\text{O}_3$  (sesquioxides) is paramagnetic in nature. It is due to presence of  
 (a) peroxide ion (b) superoxide ion  
 (c) oxide ion (d) all of these
70. Which is/are coloured and paramagnetic?  
 (a)  $\text{KO}_2$  (b)  $\text{K}_2\text{O}_3$   
 (c) Both (a) and (b) (d) None of these
71. Suboxide of Rb has the formula  
 (a)  $\text{RbO}_2$  (b)  $\text{RbO}_3$   
 (c)  $\text{Rb}_2\text{O}_2$  (d)  $\text{Rb}_6\text{O}$
72.  $\text{MO}_3$  on hydrolysis forms  
 (a)  $\text{MOH}$  and  $\text{H}_2$  (b)  $\text{MOH}$  and  $\text{O}_2$   
 (c)  $\text{MOH}$  and  $\text{M}_2\text{O}_2$  (d)  $\text{MOH}$  and  $\text{H}_2\text{O}_2$
73. Which is used as a treatment for bipolar disorder (an illness that involves alternating periods of depression)?  
 (a)  $\text{Li}_2\text{CO}_3$  (b)  $\text{K}_2\text{CO}_3$   
 (c)  $\text{LiCl}$  (d)  $\text{LiCH}_3$
74.  $\text{NaNO}_3$  is converted to  $\text{KNO}_3$  by following reaction :  

$$\text{NaNO}_3(\text{aq}) + \text{KCl}(\text{aq}) \rightleftharpoons \text{KNO}_3(\text{aq}) + \text{NaCl}(\text{s})$$
  
 In the above equilibrium, which is least soluble in hot water?  
 (a)  $\text{NaNO}_3$  (b)  $\text{KCl}$   
 (c)  $\text{KNO}_3$  (d)  $\text{NaCl}$
75. Gun powder spontaneously react when ignited. Reaction can be  
 (a)  $2\text{KNO}_3(\text{s}) + 4\text{C}(\text{s}) \longrightarrow \text{K}_2\text{CO}_3(\text{s}) + 3\text{CO}(\text{g}) + \text{N}_2(\text{g})$   
 (b)  $2\text{KNO}_3(\text{s}) + 2\text{S}(\text{s}) \longrightarrow \text{K}_2\text{SO}_4(\text{s}) + \text{SO}_2(\text{g}) + \text{N}_2(\text{g})$   
 (c) both (a) & (b)  
 (d) None of the above

### One or More Than One Options Correct

- Select correct statement(s).  
 (a)  $\text{MO}_2$  contains the paramagnetic ion  $\text{O}_2^-$   
 (b)  $\text{O}_2^-$  is stable only in the presence of large cations as K, Rb and Cs  
 (c)  $\text{KO}_2$  is paramagnetic and has orange colour  
 (d)  $\text{K}_2\text{O}$  has antifluorite structure
- Recently sodium naphthenide ( $\text{C}_{10}\text{H}_8\text{Na}$ ) has been used as reductant in complex formation.  $\text{C}_{10}\text{H}_8\text{Na}$  is  
 (a) paramagnetic (b) deep-green in colour  
 (c) diamagnetic (d) colourless
- Sesquioxides ( $\text{M}_2\text{O}_3$ ) of alkali metals  
 (a) have been prepared by careful thermal decomposition of  $\text{MO}_2$   
 (b) are dark-coloured paramagnetic substances  
 (c) are colourless diamagnetic substances  
 (d) are coloured diamagnetic substance
- Select correct statement(s).  
 (a) Alkali metals ozonides are coloured and paramagnetic  
 (b) Alkali metal-ozonides are colourless and diamagnetic  
 (c) Sesquioxides of alkali metals are peroxides disuperoxides  $(\text{M}^+)_4(\text{O}_2^{2-})(\text{O}_2^-)_2$   
 (d) Sesquioxides are paramagnetic due to presence of superoxide ion  $\text{O}_2^-$ .

## 5. Select correct alternate(s).

- (a) In  $\text{NaHCO}_3$ , the  $\text{HCO}_3^-$  ions are linked into infinite chain
- (b) In  $\text{KHCO}_3$ , a dimer is formed by H-bonding.
- (c) In  $\text{NaHCO}_3$ , a dimer is formed by H-bonding
- (d) In  $\text{KHCO}_3$ , the  $\text{HCO}_3^-$  ions are linked into infinite chain

## 6. Select correct alternate(s).

- (a) All alkali metals form solid bicarbonates
- (b) Except  $\text{LiHCO}_3$ , all alkali metals bicarbonates are solid
- (c)  $\text{Li}_2\text{CO}_3$  decomposes into  $\text{CO}_2$  and  $\text{Li}_2\text{O}$
- (d)  $\text{Na}_2\text{CO}_3$  decomposes into  $\text{CO}_2$  and  $\text{Na}_2\text{O}$

## 7. Select correct alternate(s).

- (a) Solid  $\text{LiNO}_3$  and  $\text{NaNO}_3$  are deliquescent
- (b)  $\text{KNO}_3$  is used in preference to  $\text{NaNO}_3$  in gun powder
- (c)  $\text{NaNO}_3$  is used in preference to  $\text{NaNO}_3$  in gun powder
- (d)  $\text{NH}_4\text{HCO}_3$  exists in solid state

8.  $\text{LiAlH}_4$  can reduce

- (a) carbonyl compounds into alcohols
- (b) alkenes into alkanes
- (c)  $-\text{CHO}$  group into  $-\text{CH}_3$
- (d) either into alcohols

## 9. Select correct statement(s).

- (a) Radius of hydrated  $\text{Li}^+$  ion is smaller than that of hydrated  $\text{Cs}^+$  ion
- (b) Ionic mobility of hydrated  $\text{Li}^+$  ion is smaller than that of hydrated  $\text{Cs}^+$  ion
- (c) Hydrated  $\text{Cs}^+$  is more conducting than hydrated  $\text{Na}^+$  ion
- (d) Ionic mobility of hydrated  $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$

## 10. Li does not resemble other alkali metals in following properties

- (a)  $\text{Li}_2\text{CO}_3$  decomposes into oxides while other alkali carbonates are thermally stable
- (b)  $\text{LiCl}$  is predominantly covalent
- (c)  $\text{Li}_3\text{N}$  is stable
- (d)  $\text{LiCl}$  is non-conducting in molten state

## 11. Alkali metals resemble 1B (copper family) in following respects

- (a) +1 valency
- (b) sulphates are water soluble
- (c) oxides are strong bases
- (d) oxides are strong acids

12.  $\text{Na}^+$  and  $\text{Ag}^+$  differ in

- (a)  $\text{Na}_2\text{CO}_3$  is thermally stable while  $\text{Ag}_2\text{CO}_3$  decomposes into  $\text{Ag}$ ,  $\text{CO}_2$  and  $\text{O}_2$
- (b)  $\text{Ag}^+$  forms complexes,  $\text{Na}^+$  does not
- (c)  $\text{NaCl}$  is water soluble,  $\text{AgCl}$  is insoluble
- (d)  $\text{NaCl}$  and  $\text{AgCl}$  both give colour in flame when ignited

## 13. Which is/are true statement(s)?

- (a) The heats of hydration of the divalent alkaline earth metal ions decrease with an increase in their ionic size
- (b) Hydration of alkali metal ion is less than that of IIA.
- (c) Alkaline earth metal ions, because of their much larger charge to size ratio exert a much stronger electrostatic attraction on the oxygen of water molecule surrounding them
- (d) None of the above statements is correct

## 14. Which are true statements about s-block elements?

- (a) Metals are obtained by the electrolysis of fused chlorides
- (b) Oxides are basic except  $\text{BeO}$
- (c) +1 valency by alkali metals and +2 valency by alkaline earth metals is shown
- (d) Carbonates are thermally stable

15.  $\text{Li}_2\text{CO}_3$  is

- (a) added to bauxite in the electrolytic production of aluminium
- (b) used to toughen glass
- (c) used as medicine as it affects the balance between  $\text{Na}^+$  and  $\text{K}^+$ , and  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$
- (d) thermally stable

## Passage Comprehension Questions

## Passage 1

Read the following passage and answer the questions at the end of it.

Dilute solutions of alkali metals in liquid  $\text{NH}_3$  are blue. It is the ammoniated electron which is responsible for the blue colour of the solution, and the electrical conductivity is due to the ammoniated cation,  $[\text{M}(\text{NH}_3)_x]^+$  as well as the ammoniated electron,  $[\text{e}(\text{NH}_3)_y]^-$ , values of  $x$  and  $y$  depend on the extent of solvation (by  $\text{NH}_3$ ). Dilute solutions are paramagnetic due to free electrons.

## 1. What happens if alkali metal is allowed to react with concentrated ammonia solution?

- (a) Paramagnetic character of solvated electrons is retained
- (b) Solvated electrons associate to form electron-pairs and paramagnetic character decreases
- (c) Reducing character is increased
- (d) Reducing character is not affected

## 2. Ammoniated solutions of alkali metals are reducing agents due to the presence of free or solvated electrons and can reduce

- (a)  $\text{O}_2$  to  $\text{O}_2^{2-}$
- (b)  $\text{K}_2[\text{Ni}(\text{CN})_4]$  to  $\text{K}_4[\text{Ni}(\text{CN})_4]$
- (c) both (a) & (b)
- (d) none of the above

### Passage 2

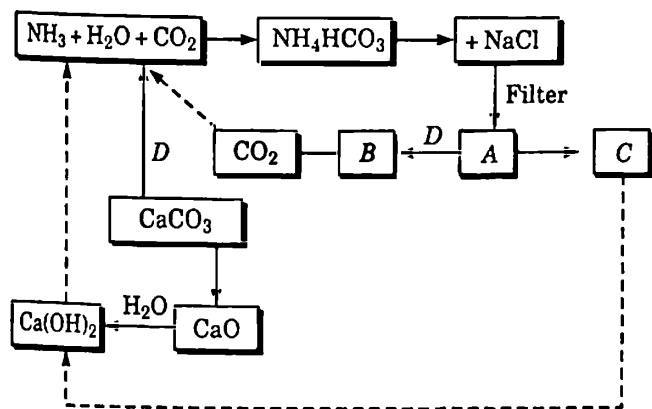
Questions given below are based on the following values of hydration energy and lattice energy.

| Hydration energy<br>$\Delta H_{\text{hydr.}} (\text{kJ mol}^{-1})$ |      | Lattice energy<br>$\Delta H_L (\text{kJ mol}^{-1})$ |      |
|--------------------------------------------------------------------|------|-----------------------------------------------------|------|
| $\text{Li}^+$                                                      | -499 | $\text{LiCl}$                                       | -840 |
| $\text{Na}^+$                                                      | -390 | $\text{NaCl}$                                       | -776 |
| $\text{K}^+$                                                       | -305 | $\text{KCl}$                                        | -703 |
| $\text{Cl}^-$                                                      | -382 |                                                     |      |

- Which salt has maximum heat of hydration?  
(a)  $\text{LiCl}$  (b)  $\text{NaCl}$   
(c)  $\text{KCl}$  (d)  $\text{LiCl}$  and  $\text{KCl}$  equally
- Heat of hydration (numerical value) of  $\text{LiCl}$ ,  $\text{NaCl}$  and  $\text{KCl}$  in the increasing order is  
(a)  $\text{LiCl} < \text{KCl} < \text{NaCl}$  (b)  $\text{LiCl} < \text{NaCl} < \text{KCl}$   
(c)  $\text{LiCl} = \text{KCl} < \text{NaCl}$  (d)  $\text{KCl} < \text{NaCl} < \text{LiCl}$
- Maximum heat is absorbed in the dissolution of one mole of  
(a)  $\text{LiCl}$  (b)  $\text{NaCl}$   
(c)  $\text{KCl}$  (d) equally
- Which salt can be used to control humidity?  
(a)  $\text{LiCl}$  (b)  $\text{NaCl}$   
(c)  $\text{KCl}$  (d) None of these

### Passage 3

Answer the questions based on following flow-sheet.

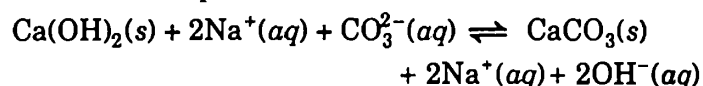


- This flow-sheet represents  
(a) Solvay process of  $\text{NaOH}$   
(b) Solvay process of  $\text{Na}_2\text{CO}_3$   
(c) Dow process of  $\text{Na}_2\text{CO}_3$   
(d) none of the above is correct
- Filtrate A contains  
(a)  $\text{NH}_4\text{Cl}$  (b)  $\text{Na}_2\text{CO}_3$   
(c)  $\text{NaHCO}_3$  (d)  $\text{CaCO}_3$
- Species B formed is  
(a)  $\text{NH}_3$  (b)  $\text{CO}_2$   
(c)  $\text{Na}_2\text{CO}_3$  (d)  $\text{NaHCO}_3$
- Following are some statements about species C. Select correct statement(s).  
(a) C is  $\text{NH}_4\text{Cl}$   
(b) C is  $\text{NaHCO}_3$   
(c) C is recycled into  $\text{Ca(OH)}_2$  chamber to form  $\text{NH}_3$   
(d) C is  $\text{Na}_2\text{CO}_3$
- Reaction given in the passage is spontaneous because  
(a)  $\text{NaOH}$  formed is ionic  
(b)  $\text{CaCO}_3$  is removed from the reaction mixture  
(c) reaction is exothermic  
(d) reaction is endothermic
- $\text{NaOH}$  can also be prepared by electrolysis of aqueous  $\text{NaCl}$ . Amount of  $\text{NaOH}$  formed when 0.445 L of  $\text{NaCl}$  (aq) is electrolysed for 137 s with a current of 1.08 A, is  
(a) 0.09 g  
(b) 0.12 g  
(c) 0.06 g  
(d) amount of  $\text{NaCl}$  has not been given
- pH of the above solution (in Q. 5) is  
(a) 11.70 (b) 11.53  
(c) 11.83 (d) data is incomplete

### Passage 4

Read the following passage and answer the questions given at the end.

One of the chief uses of sodium carbonate has been in the conversion of  $\text{Ca(OH)}_2(\text{s})$  to concentrated aqueous solution of  $\text{NaOH}$  which in turn was used in the manufacture of soap



In 1775, in order to gain independence from the importation of natural  $\text{Na}_2\text{CO}_3$ , the French government offered a prize to any one who could devise a process to prepare  $\text{Na}_2\text{CO}_3$  from  $\text{NaCl}$ .

- Who first devised a process of preparing  $\text{Na}_2\text{CO}_3$  from  $\text{NaCl}$ ?  
(a) Solvay (b) Nicolas Leblanc  
(c) Peterson (d) Hofmann
- A more economical process but based on same principle was given by  
(a) Solvay (b) Leblanc  
(c) Williamson (d) Haber
- What is natural source of  $\text{Na}_2\text{CO}_3$ ?  
(a) Nitre  
(b) Chile salt peter  
(c) Dolomite  
(d) Trona
- Reaction given in the passage is spontaneous because  
(a)  $\text{NaOH}$  formed is ionic  
(b)  $\text{CaCO}_3$  is removed from the reaction mixture  
(c) reaction is exothermic  
(d) reaction is endothermic
- $\text{NaOH}$  can also be prepared by electrolysis of aqueous  $\text{NaCl}$ . Amount of  $\text{NaOH}$  formed when 0.445 L of  $\text{NaCl}$  (aq) is electrolysed for 137 s with a current of 1.08 A, is  
(a) 0.09 g  
(b) 0.12 g  
(c) 0.06 g  
(d) amount of  $\text{NaCl}$  has not been given
- pH of the above solution (in Q. 5) is  
(a) 11.70 (b) 11.53  
(c) 11.83 (d) data is incomplete

### Passage 5

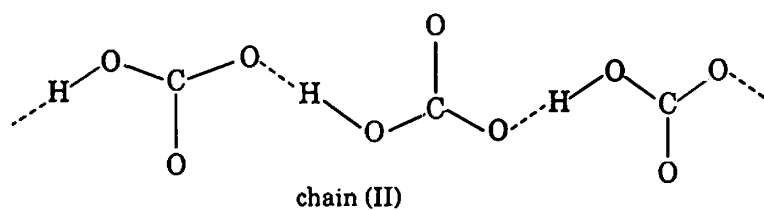
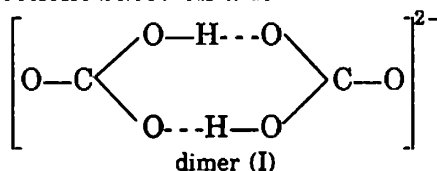
$\text{NaHCO}_3$  can be used on its own to make cakes or bread "rise". Baking powder is more commonly used, and contains  $\text{NaHCO}_3$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and starch. An improved combination baking powder contains about 40% starch, 30%  $\text{NaHCO}_3$ , 20%  $\text{NaAl}(\text{SO}_4)_2$  and 10%  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ .

Answer the following questions based on above study.

- Rise in bread and cakes is due to ..... when it decomposes between  $50^\circ\text{C}$  and  $100^\circ\text{C}$ 
  - $\text{CO}_2$
  - $\text{H}_2\text{O}$
  - both (a) and (b)
  - None of these
- $\text{Ca}(\text{H}_2\text{PO}_4)_2$  in baking powder
  - behaves as an acid in moist condition and decomposes  $\text{NaHCO}_3$  to give  $\text{CO}_2$
  - behaves as a base in moist condition and gives  $\text{H}_3\text{PO}_4$
  - behaves as a binder
  - behaves as a filler
- Filler in baking powder is
  - $\text{NaHCO}_3$
  - $\text{Ca}(\text{H}_2\text{PO}_4)_2$
  - starch
  - $\text{NaAl}(\text{SO}_4)_2$
- In improved baking powder,  $\text{NaAl}(\text{SO}_4)_2$ 
  - makes the decomposition of  $\text{NaHCO}_3$  faster
  - slows the decomposition of  $\text{NaHCO}_3$
  - acts as filler
  - makes the bread rise

### Passage 6

The crystal structures of  $\text{NaHCO}_3$  and  $\text{KHCO}_3$  both show hydrogen bonding, but are different. Answer the following questions based on this



- Which structure is adopted by  $\text{NaHCO}_3$  ?
  - I
  - II
  - Both of these
  - None of these
- Which structure is adopted by  $\text{KHCO}_3$  ?
  - I
  - II
  - Both of these
  - None of these
- Which is used in baking powder?
  - $\text{LiHCO}_3$
  - $\text{NaHCO}_3$
  - $\text{KHCO}_3$
  - $\text{Na}_2\text{CO}_3$

### Passage 7

Sesquioxides " $\text{M}_2\text{O}_3$ " have been prepared for K, Rb and Cs. Ozonides  $\text{MO}_3$  have been prepared for Na, K, Rb and Cs. Answer the following questions.

- Which are paramagnetic in nature?
  - $\text{M}_2\text{O}_3$ ,  $\text{MO}_3$ ,  $\text{MO}_2$
  - $\text{M}_2\text{O}_2$ ,  $\text{M}_2\text{O}$
  - Both (a) & (b)
  - None of these cases
- Sesquides is said to be double oxide of
  - oxide, peroxide
  - oxide, superoxide
  - peroxide, disuperoxide
  - oxide, disuperoxide
- A typical sesquioxide of Rb/Rb $_4\text{O}_6$  can be represented as
  - $[\text{Rb}_4(\text{O}_2^{2-})(\text{O}_2^-)_2]$
  - $\text{Rb}_4(\text{O}_2^{2-})_6$
  - $\text{RbO}_2 \cdot (\text{Rb}_2\text{O}_2)_2$
  - $\text{Rb}_2\text{O} \cdot (\text{Rb}_2\text{O}_2)_2$

### Passage 8

Reduction potentials of group 1 (alkali metals) are given below :

| Element                                       | $E^\circ (V)$ |
|-----------------------------------------------|---------------|
| $\text{Li}^+ + e^- \longrightarrow \text{Li}$ | -3.045        |
| $\text{Na}^+ + e^- \longrightarrow \text{Na}$ | -2.714        |
| $\text{K}^+ + e^- \longrightarrow \text{K}$   | -2.925        |
| $\text{Rb}^+ + e^- \longrightarrow \text{Rb}$ | -2.925        |
| $\text{Cs}^+ + e^- \longrightarrow \text{Cs}$ | -2.923        |

Answer the following questions.

- Which is the best reducing agent?
  - Li
  - Na
  - Rb
  - Cs
- Which is the poorest reducing agent?
  - Li
  - Na
  - Rb
  - Cs
- $E^\circ$  can be related to
  - $\Delta G^\circ$
  - $\Delta H^\circ$
  - both (a) and (b)
  - None of these
- $\text{Li}(s) \longrightarrow \text{Li}^+(aq) + e^-$  involved
  - sublimation
  - ionisation
  - hydration
  - all of these

### Assertion & Reason

Codes :

- Both **A** and **R** are true and **R** is the correct explanation of **A**.
  - Both **A** and **R** are true but **R** is not the correct explanation of **A**.
  - A** is true but **R** is false.
  - A** is false but **R** is true.
1. **Assertion (A):**  $\text{Li}^+$  forms series of trihydrates  $\text{LiX} \cdot 3\text{H}_2\text{O}$  [ $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{ClO}_2, \text{ClO}_4, \text{MnO}_4, \text{NO}_3, \text{BF}_4$ ]  
**Reason (R):** This is due to its smaller size ( $\text{Li}^+$ ) and highest ion dipole interaction.

2. **Assertion (A)** : Lithium does not form alums.

**Reason (R)** : Small  $[\text{Li}(\text{H}_2\text{O})_6]^+$  is too small to form a stable lattice required for alum formation.

3. **Assertion (A)** : Alkali metals form solid bicarbonates.

**Reason (R)** :  $\text{LiHCO}_3$  exists in aqueous solution.

4. **Assertion (A)** :  $\text{NH}_4\text{HCO}_3$  exists in solid state.

**Reason (R)** : Alkali metals form solid bicarbonates.

5. **Assertion (A)** :  $\text{NaHCO}_3$  and  $\text{KHCO}_3$  exist in solid state.

**Reason (R)** : Alkali metal ions are basic in nature.

6. **Assertion (A)** :  $\text{K}_2\text{CO}_3$  cannot be prepared by solvay process.

**Reason (R)** :  $\text{KHCO}_3$  being fairly soluble in water does not precipitate in carbonation tower.

7. **Assertion (A)** :  $\text{CsF}_2$  could not be formed from its elements.

**Reason (R)** : Enthalpy of formation of  $\text{CsF}$  is much larger which makes  $\text{CsF}_2$  unstable.

8. **Assertion (A)** : The superoxide  $\text{MO}_2$  contains the paramagnetic ion  $\text{O}_2^-$ .

**Reason (R)** :  $\text{O}_2^-$  is stable in presence of large cations as K, Rb, Cs.

9. **Assertion (A)** :  $\text{FrCl}$  has  $\text{CsCl}$  structure with coordination number 8.

**Reason (R)** : CN 8 is favoured by the large cation size.

10. **Assertion (A)** : Fr burns in air forming  $\text{FrO}_2$ .

**Reason (R)** : The larger alkali metal ions stabilise  $\text{O}_2^-$  (superoxide).

11. **Assertion (A)** :  $\text{FrClO}_4$  and  $\text{Fr}_2\text{PtCl}_6$  are the salts of low solubility.

**Reason (R)** : All alkali metal ions form insoluble salts.

12. **Assertion (A)** : Li is used in photocells.

**Reason (R)** : Cs has lower ionisation energy than Li.

13. **Assertion (A)** : The mobility of sodium ion is lower than that of potassium ion.

**Reason (R)** : The ionic mobilities depend on the effective radius of the ion.

14. **Assertion (A)** : Among the alkali metals, lithium salts exhibit the least electrical conductance in aqueous solutions.

**Reason (R)** : Smaller the radius of the hydrated cation, lower is the electrical conductance in aqueous solutions.

15. **Assertion (A)** : Ether can extract  $\text{LiCl}$  from the aqueous solution of a mixture of  $\text{LiCl}$ ,  $\text{NaCl}$  and  $\text{KCl}$ .

**Reason (R)** : Hydration of  $\text{Li}^+$  ion is greater than that of  $\text{Na}^+$  and  $\text{K}^+$  ions.

16. **Assertion (A)** :  $\text{NaOH}$  cannot be stored in a vessel made of Al or Zn.

**Reason (R)** : A protective layer of oxide is formed on the surface of the metal.

## True & False

1.  $\text{K}_2\text{O}_2$  is paramagnetic but  $\text{KO}_2$  is diamagnetic.
2. When aqueous  $\text{KO}_2$  solution reacts with  $\text{CO}_2$ ,  $\text{O}_2$  is formed thus  $\text{KO}_2$  is used in submarines.
3. Borax or microcosmic salt can be used to identify coloured cations.
4.  $\text{Li}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  are thermally stable.
5. When 1 mole of  $\text{Na}_2\text{CO}_3$  is heated strongly, 1 mole of  $\text{CO}_2$  is formed.
6. Solution of Na in liquid  $\text{NH}_3$  is of blue colour due to solvated electron.
7. Lattice energy of alkali metal chlorides is in order:  
 $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl} > \text{CsCl}$
8.  $\text{LiHCO}_3$  does not exist in solid state.
9. Polarising power of  $\text{Li}^+$  ion is nearly the same as that of  $\text{Mg}^{2+}$  ion.
10. Alkali metals form covalent hydrides.
11. The enthalpy of hydration decreases in going from  $\text{Li}^+$  to  $\text{Cs}^+$ .
12. Potassium burns in air forming potassium superoxide.
13. Aqueous solution of brine on electrolysis forms sodium.
14. Carnallite is  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .
15.  $\text{Li}_2\text{SO}_4$  forms double salts with  $\text{Al}_2(\text{SO}_4)_3$ .
16.  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$  is insoluble in water.
17.  $\text{KHCO}_3$  is less soluble than  $\text{NaHCO}_3$  and is thus prepared easily by following reaction.  
$$\text{NH}_4\text{HCO}_3 + \text{KCl} \longrightarrow \text{NH}_4\text{Cl} + \text{KHCO}_3$$
18. Alkali metal hydrides are ionic in nature.
19. The solubility of carbonates and bicarbonates of alkali metals increases down the group.
20. Zinc displaces  $\text{H}_2$  on reaction with aqueous  $\text{NaOH}$  as well as with dil.  $\text{HCl}$ .

## Fill in the Blanks

- ..... of IA and ..... of IIA show diagonal relationship.
- ..... is binary oxide of alkali metal.
- NaOH can't be stored in the vessel made of .....
- ..... can react with NaOH as well as with HCl. This salt gives  $\text{CO}_2$  on heating.
- The fact that Li has maximum reducing nature is due to its maximum negative ..... value which is actually in aqueous solution  $M^+(aq) + e^- \longrightarrow M(s)$ .
- The first element of a group in many ways differs from the other heavier members of the group. These differences arise on account of three factors :  
(i) ..... (ii) ..... (iii) .....
- Alkali metals dissolve in liquid ammonia to give ..... coloured solutions which upon standing slowly liberate  $\text{H}_2$ . The ..... colour of metal-ammonia solutions is due to the presence of ..... electrons.
- Of the alkali metals only ..... forms nitrides.
- Of the alkali metal carbonates, only ..... decomposes to give  $\text{CO}_2$  and metal oxide.
- Alkali metal and alkaline earth metal chlorides can be detected by ..... test.
- $\text{KO}_2$  is ..... absorber and ..... producer and is thus used in .....
- A solute dissolves in water if  $\Delta H_{\text{hydration}}$  is ..... than  $\Delta H_U$ .
- Of the  $\text{O}_2^-$ ,  $\text{O}_2^{2-}$  and  $\text{O}_2$ , ..... has odd order bond and, ..... and ..... are paramagnetic.
- ..... is used to control humidity.
- $\text{Li}_3\text{N}$  is decomposed by water forming ..... gas.
- Lithium ion has the ..... hydration enthalpy of all the alkali metals.
- Alkali metals are good ..... agents.
- The phenomenon of crumbling to powder of sodium carbonate crystals on exposure to air is called .....
- Potassium salts impart ..... colour to the flame.
- Aqueous solution of  $\text{Na}_2\text{CO}_3$  is ..... due to ..... of .....
- $\text{RCOOH}$  decomposes  $\text{NaHCO}_3$  to liberate  $\text{CO}_2$  which comes from .....
- Sodium metals when dissolved in ammonia gives a ..... solution.
- Sodium metal when dissolved in ammonia conducts electricity because of .....

- Sodium silicate dissolved in water, and its concentrated aqueous solution is called .....
- The Castner's process uses molten ..... for the extraction of sodium.

## Matrix-Match Type Questions

### I. Only One Correct

- Match the commercial names (in List I) with the chemical formulae (in List II).

| List I            | List II                                                |
|-------------------|--------------------------------------------------------|
| A. Caustic potash | 1. $\text{Na}_2\text{CO}_3$                            |
| B. Common salt    | 2. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ |
| C. Soda ash       | 3. NaCl                                                |
| D. Lithia         | 4. KOH                                                 |
| E. Caustic soda   | 5. $\text{NaHCO}_3$                                    |
| F. Baking soda    | 6. $\text{KNO}_3$                                      |
| G. Glaubers' salt | 7. $\text{Li}_2\text{O}$                               |
| H. Salt petre     | 8. NaOH                                                |

- Select the metals (in List I) with the specific properties of the compounds (in List II).

| List I | List II                                           |
|--------|---------------------------------------------------|
| A. Li  | 1. Super oxide                                    |
| B. Na  | 2. Lewis acid—a chloride                          |
| C. K   | 3. Most negative value of $E_{\text{redn}}^\circ$ |
| D. Be  | 4. Thermally stable carbonate                     |
| E. Mg  | 5. No flame colouration of the chloride           |

- Match List I (Compounds) with List II (Associated Uses).

| List I<br>(Compounds) | List II (Associated Uses) |
|-----------------------|---------------------------|
| A. $\text{KO}_2$      | 1. Baking                 |
| B. $\text{NaHCO}_3$   | 2. Photovoltaic cell      |
| C. LiCl               | 3. Submarine              |
| D. Cs                 | 4. Humidity control       |

### II. One or More Correct

- Match the species in Column I with given property (ies) in Column II.

| Column I                      | Column II              |
|-------------------------------|------------------------|
| A. Alkalide of halonium       | 1. Paramagnetic        |
| B. Superoxide of alkali metal | 2. Diamagnetic         |
| C. Peroxide of alkali metal   | 3. Life saving devices |
| D. Oxide of alkali metal      | 4. Oxidant             |
|                               | 5. Bleaching agent     |
|                               | 6. Dissolves Zn, Al    |

2. Match the species in Column I with given property (ies) in Column II.

| Column I                   | Column II               |
|----------------------------|-------------------------|
| A. $\text{Li}_3\text{N}$   | 1. Paramagnetic         |
| B. $\text{LiCl}$           | 2. Ether soluble        |
| C. $\text{KO}_2$           | 3. Humidity control     |
| D. $\text{Rb}_2\text{O}_3$ | 4. Automobiles air bags |
|                            | 5. Coloured compounds   |

## Integer Answer Types

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the ORS have to be darkened. For example, if the correct answers to question number X, Y, Z and W (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will be like the following :

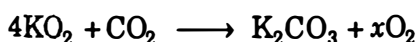
| X | Y | Z | W |
|---|---|---|---|
| ① | ① | ① | ① |
| ② | ② | ② | ② |
| ③ | ③ | ③ | ③ |
| ④ | ④ | ④ | ④ |
| ⑤ | ⑤ | ⑤ | ⑤ |
| ⑥ | ⑥ | ⑥ | ⑥ |
| ⑦ | ⑦ | ⑦ | ⑦ |
| ⑧ | ⑧ | ⑧ | ⑧ |
| ⑨ | ⑨ | ⑨ | ⑨ |

### Set I

- Unpaired electron(s) in superoxide ion .....
- Potassium sesquioxide has actually ..... O atoms
- When one mole of  $\text{Na}_2\text{CO}_3$  is heated,  $\text{CO}_2$  obtained is ..... mole.
- Number of  $\text{HCO}_3^-$  ions joined by H-bonding in  $\text{KHCO}_3$  is .....
- When  $\text{LiNO}_3$  is heated, change in oxidation number of N is .....
- When  $\text{NaNO}_3$  is heated, change in oxidation number of N is .....
- Number of s-electrons in  $\text{Na}^+$  is .....
- Number of elements in second period showing diagonal relationship is .....

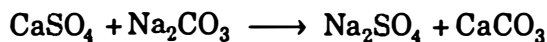
### Set II

- Number of radioactive elements in s-block is .....
- Hydrated sodium sulphite has 50%  $\text{H}_2\text{O}$ . Number of molecules of hydration is .....
- One mole of lithium nitride is decomposed by  $\text{H}_2\text{O}$  and resultant solution is neutralised by  $\text{HCl}$ . Number of moles of  $\text{HCl}$  required is .....
- $\text{Cl}_2$  disproportionates to  $\text{NaCl}$  and  $\text{NaClO}_3$  on passing into hot  $\text{NaOH}$  solution. In this process each mole of  $\text{Cl}_2$  consumes ..... mole(s) of  $\text{NaOH}$ .
- $\text{KO}_2$  is  $\text{CO}_2$  absorber and  $\text{O}_2$  producer as shown



Value of x is .....

6.  $\text{Na}_2\text{CO}_3$  removes permanent hardness :



10 L of hard water required 0.0848 g  $\text{Na}_2\text{CO}_3$ . Thus, hardness in ppm of  $\text{CaCO}_3$  is .....

- Potassium superoxide has ..... unpaired electron(s).
- Bond order of oxide in sodium peroxide is .....

## Test Yourself on Periodic Table

- Mark the element which is invariably bivalent and whose oxide is soluble in excess of  $\text{NaOH}$  and its dipositive ion has a noble gas core :

- Identify the elements in the Periodic Table:  
A : which shows diagonal relationship to Be  
B : which shows diagonal relationship to Li  
C : whose alkali metal carbonate is decomposed on heating  
D : coinage metals

- Out of the elements marked A, B, C, D, E, F, G, and H



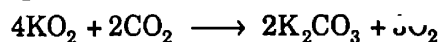
# Answers & Solutions

## Master Exercises

### Exercise 1

#### Short Answer Type Questions

1.  $\text{LiHCO}_3$
2.  $\text{KO}_2$  : It absorbs  $\text{CO}_2$  and releases  $\text{O}_2$  thus is used in life-saving devices.



It is paramagnetic due to unpaired electrons in  $\text{O}_2^-$  (superoxide ion).

3. (a) Smaller the size, larger the charge hence greater the hydration and smaller ionic conductance.

| $\text{Li}^+$ | $\text{Be}^{2+}$ |                   |
|---------------|------------------|-------------------|
| >             |                  | Size              |
| <             |                  | Charge            |
| <             |                  | Hydration         |
| >             |                  | Ionic conductance |

(b)  $\text{Li}^+ > \text{K}^+$

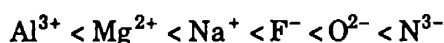
(c)  $\text{LiCl} > \text{NaCl}$  (smaller cation  $\text{Li}^+$  polarises to a greater extent than  $\text{Na}^+$ )

(d)  $\text{Na}_2\text{CO}_3 > \text{Li}_2\text{CO}_3$

(e)  $\text{Li}^+ > \text{Na}^+$

(f)  $\text{LiI} > \text{CsI}$

4.  $r_n \propto \frac{1}{Z}$  (for isoelectronic species)



5.  $\text{CsCl} < \text{RbCl} < \text{KCl} < \text{NaCl} < \text{LiCl}$

6.  $\text{Li}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{K}_2\text{CO}_3 < \text{Rb}_2\text{CO}_3$

7. A :  $\text{Na}_2\text{O}_2$

B :  $\text{H}_2\text{O}_2$

C :  $\text{CrO}_3$  (chromic anhydride blue in ethereal layer)

8.  $\text{RbClO}_4 < \text{KClO}_4 < \text{NaClO}_4 < \text{LiClO}_4$

(Due to sharp decrease in hydration energy compared to lattice energy).

9.  $\text{LiF} < \text{NaF} < \text{KF} < \text{RbF} < \text{CsF}$

With smaller ion (as  $\text{F}^-$ ) decrease in lattice energy more than decrease in hydration energy.

10. Low solubility of  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$  is used to detect potassium ion in solution in qualitative analysis.

11.  $\text{Na} \longrightarrow \text{Na}^+ + e^-$

When cation is formed, outermost shell is removed (in case of alkali metal) and also due to increase in force of attraction, outermost shell is pulled inward. Hence, ionic size decreases.

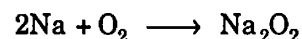
12. In aqueous solution of  $\text{LiCl}$  and  $\text{NaCl}$ , add ether.  $\text{LiCl}$  being covalent is extracted into ether. Evaporate ether when  $\text{LiCl}$  is left as residue.

13.  $\text{Li}^+ < \text{Na}^+$  (size)

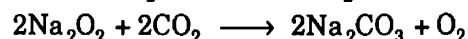
Thus, polarisation by  $\text{Li}^+$  is larger than that of  $\text{Na}^+$ . Thus,  $\text{LiCl}$  is more covalent than  $\text{NaCl}$ . Hence, m.p. of  $\text{LiCl}$  (being covalent) is lower than that of  $\text{NaCl}$ .

14. Refer text

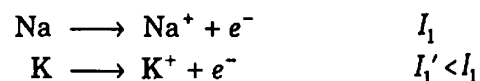
15. Oxone is the commercial name for the preparation of  $\text{Na}_2\text{O}_2$  (sodium peroxide)



$\text{Na}_2\text{O}_2$  is used in life-saving devices in submarines.  $\text{Na}_2\text{O}_2$  absorbs  $\text{CO}_2$  and releases  $\text{O}_2$



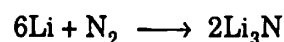
16. Along a group, ionisation energy decreases and thus tendency to oxides increases.



Thus, Na is less reactive than K.

17. Lithium has highest ionisation energy while caesium has the lowest among the alkali metals. Photoelectric cells are based on emission of electrons. Hence, Cs with least ionisation energy has better tendency (as compared to Li) to emit electrons hence thus finds use in photoelectric cells.

18.  $\text{N}^{3-}$  is very small in ionic size and thus can be set into crystalline lattice with smaller  $\text{Li}^+$  ion. Thus,  $\text{Li}_3\text{N}$  is formed



19. (a)  $\text{KO}_2$  (with superoxide as  $-1$ )

(b)  $\text{K}^+\text{O}_2^-$  thus  $K = +1$

(c)  $\text{O}_2^-(17e^-)$  has M.O. electronic configuration as  
 $\sigma 1s^2 \quad \sigma^* 1s^2 \quad \sigma 2s^2 \quad \sigma^* 2s^2 \quad \sigma 2p_z^2 \quad \pi 2p_y^2 \quad \pi 2p_x^2$   
 $\pi^* 2p_y^2 \quad \pi^* 2p_x^1$

$N_B$  = Electrons in bonding MO = 10

$N_A$  = Electrons in anti-bonding MO = 7

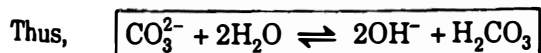
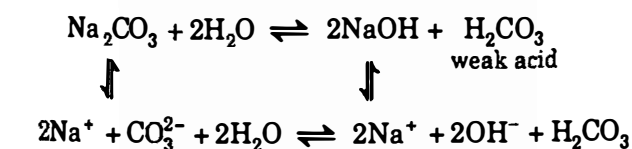
$$\text{Number of bonds} = \frac{N_B - N_A}{2} = \frac{10 - 7}{2} = 1.5$$

$$\text{Number of unpaired electron} = N = 1$$

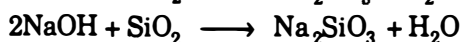
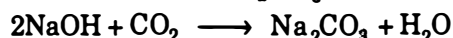
$$\begin{aligned}\text{Thus, magnetic moment} &= \sqrt{N(N+2)} \text{ BM} \\ &= \sqrt{3} \text{ BM}\end{aligned}$$

It is paramagnetic due to unpaired electron.

20.  $\text{Na}_2\text{CO}_3$  is salt of weak acid ( $\text{H}_2\text{CO}_3$ ) and strong base ( $\text{NaOH}$ ).  $\text{CO}_3^{2-}$  is hydrolysed forming free  $\text{OH}^-$  thus it is alkaline in nature



21.  $\text{NaOH}$  absorbs atmospheric  $\text{CO}_2$  and thus while deposit of  $\text{Na}_2\text{CO}_3$  is formed. Also  $\text{SiO}_2$  of glass reacts with  $\text{NaOH}$  forming insoluble  $\text{Na}_2\text{SiO}_3$  (white deposit)

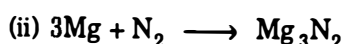
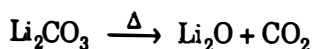
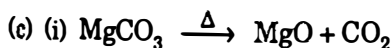


22.  $\text{KOH}$  is hygroscopic and thus absorbs  $\text{H}_2\text{O}$ . Thus,  $\text{KOH}$  pallets become wet.

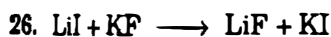
23. Lithium (density =  $0.53 \text{ g mL}^{-1}$ ) is lighter than water hence it floats on water. Being less reactive (due to high IE) it does not react with  $\text{H}_2\text{O}$  to a greater extent.

24. (a)  $\text{Li}$  resembles  $\text{Mg}$

(b)  $\text{Mg}$  belongs to group II (alkaline earth metals)



25.  $\text{Li}^+$  being smaller in size cannot stabilise larger anion as  $\text{O}_2^{2-}$  (peroxide). Thus,  $\text{Li}_2\text{O}_2$  is not formed.



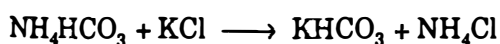
This reaction is spontaneous in forward side indicating that  $\text{Li}^+$  (smaller cation) is attached to  $\text{F}^-$  (smaller anion) and  $\text{K}^+$  (larger cation) is attached to  $\text{I}^-$  (larger anion).

27.  $\text{Li}_2\text{SO}_4$  is the only alkali metal salt that does not form double salt (as alum) as it cannot set cavity of alum.

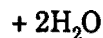
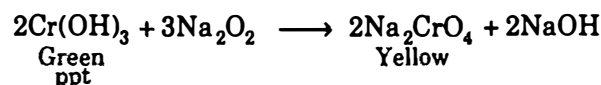
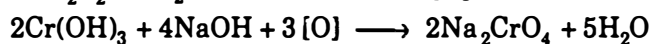
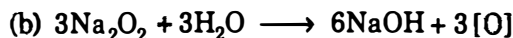
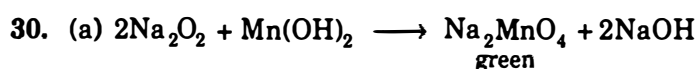
28. Baking soda and baking powder, they are different.

Baking soda is  $\text{NaHCO}_3$  and baking powder is a mixture of  $\text{NaHCO}_3$ ,  $\text{Ca}(\text{HPO}_4)_2$  starch and potassium hydrogen tartrate.

29. In Solvay process, intermediate reactions are



$\text{KHCO}_3$  is highly soluble in water and cannot be separated by crystallisation.



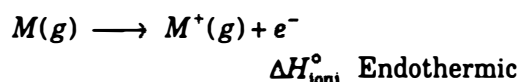
## Analytical Questions

1. The oxidation of a metal ( $M$ ) to form  $M^+(aq)$  takes place in following stages :

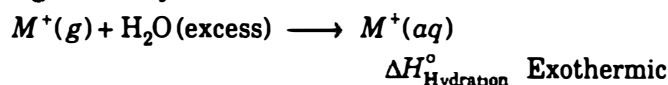
Stage I : Sublimation



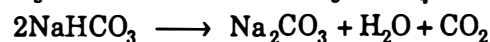
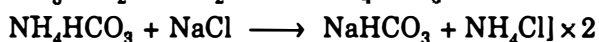
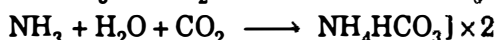
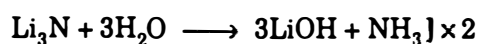
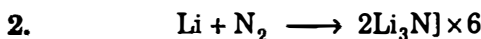
Stage II : Ionisation



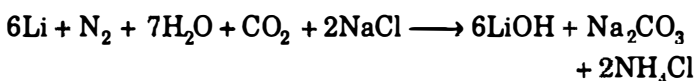
Stage III : Hydration



It is feasible only if more energy is released in stage III than that absorbed in stages I and II.  $\text{Li}^+$  being smallest in size, its hydration is maximum hence energy released in stage III (exothermic) is much larger than that absorbed overall in stages I and II together. Thus,  $\text{Li}$  acts as strongest reducing agent and is the best reducing agent.



Overall



Thus, every one mole of  $\text{N}_2$  gives enough  $\text{NH}_3$  that can be used to absorb  $\text{CO}_2$  and thus gives one mole  $\text{Na}_2\text{CO}_3$



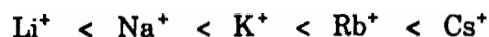
$$1 \text{ mole} \equiv 1 \text{ mole}$$

$$22.4 \text{ L at NTP} \equiv 106 \text{ g}$$

$$22.4 \text{ kL at NTP} \equiv 10.6 \text{ kg}$$

Thus,  $22.4 \times 10^3 \text{ L N}_2$  is required.

3. (a) Greater the charge, smaller the radius, larger the hydration and thus heavier (hydrated) ion more slower.



ionic size  $\longrightarrow$  max

hydration  $\longleftarrow$  max

Ionic mobility  $\longrightarrow$  max



## Exercise 2

## Only One Option Correct

1. (a)  $[\text{Ar}] 3d^{10} 4s^2$  — Last filling electron is in  $3d$  thus it is  $d$ -block element

(b)  $[\text{Ar}] 3d^{10} 4s^1$  — same as (a)

Thus, both are  $d$ -block element

Thus, (c)

2. (a)  $\text{Li}_2\text{CO}_3 \xrightarrow{\Delta} \text{Li}_2\text{O} + \text{CO}_2$  |  $\text{Na}_2\text{CO}_3 \xrightarrow{\Delta} X$

Thus, (a) is true

(b)  $\text{LiCl}$  soluble in ether thus covalent |  $\text{NaCl}$  insoluble in ether but soluble in  $\text{H}_2\text{O}$  thus ionic

Thus, (b) is true

(c)  $\text{Li}$  forms nitride |  $\text{Na}$  does not form nitride

Thus, (c) is true

Thus, (d)

| 3. IA (Alkali)                                                                             | IB (Coinage)                                                                                   |
|--------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| (a) $\text{NaCl}$                                                                          | $\text{CuCl} + 1$ valency<br>thus true                                                         |
| (b) $\text{Na}_2\text{SO}_4$ soluble                                                       | $\text{CuSO}_4, \text{Ag}_2\text{SO}_4$<br>less soluble                                        |
| (c) $\text{Na}_2\text{O} + \text{H}_2\text{O} \longrightarrow 2\text{NaOH}$<br>strong base | $\text{Cu}_2\text{O} + \text{H}_2\text{O} \longrightarrow \text{Cu}(\text{OH})_2$<br>weak base |
| (d) also false                                                                             | Thus false                                                                                     |

Thus, (a)

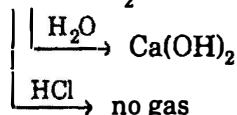
4.  $\text{NaCl}$  — golden yellow

$\text{AgCl}$  — no flame

Thus, (d) is incorrect

5. (a)  $\text{Na}_2\text{CO}_3 \xrightarrow{\Delta} \text{no CO}_2$

(b)  $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$



(c)  $\text{Ca}(\text{HCO}_3)_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$   
insoluble in  $\text{H}_2\text{O}$

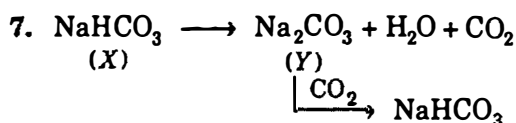
(d)  $2\text{NaHCO}_3 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$   
 $\xrightarrow{\text{HCl}} \text{CO}_2 \uparrow$

$\text{Na}_2\text{CO}_3$  is water soluble

Thus, (d)

6.  $\text{KO}_2$  is stable due to larger anion  $\text{O}_2^-$  which polarises  $\text{K}^+$

Thus, (b)



Thus, (c)

8. (c) 9. (c)

10. In molten state  $\text{NaCl}(l) \rightleftharpoons \text{Na}^+ + \text{Cl}^-$

Thus, (b)

11. (d)

12.  $\text{Na}_2\text{CO}_3 + \text{SO}_2 \longrightarrow \text{Na}_2\text{SO}_3 + \text{CO}_2$

Thus, (d)

13.  $\text{Na}_2\text{CO}_3$  is thermally stable

Thus, (a)

14. Alkali salts are colourless

$\text{NaCl}$  colourless  $\text{Na}_2\text{CrO}_4$  — yellow since  $\text{CrO}_4^{2-}$  is yellow

$\text{KCl}$  colourless  $\text{K}_2\text{CrO}_4$  — yellow  
 $\text{KMnO}_4$  — pink since  $\text{MnO}_4^-$  is pink  
 $\text{K}_2\text{MnO}_4$  — green since  $\text{MnO}_4^{2-}$  is green

Thus, (b)

15.  $\text{Na} + \text{O}_2 \longrightarrow \text{Na}_2\text{O}$

$\text{Li} + \text{O}_2 \longrightarrow \text{Li}_2\text{O}$

$\text{Li} + \text{N}_2 \longrightarrow \text{Li}_3\text{N}$

Thus, (d)

16.  $\text{Li}$  and  $\text{Na}$  do not form superoxide  $\text{MO}_2$

Thus, (b)

17. (a)

18.  $4\text{KO}_2 + 2\text{H}_2\text{O} + 4\text{CO}_2 \longrightarrow 4\text{KHCO}_3 + 3\text{O}_2$

Thus, (a)

19. Third IE ( $I_3$ ) is very high, thus it represents alkali earth metal ( $\text{Be}$ )

Thus, (c)

20.  $2\text{Na}_2\text{O}_2 + 2\text{CO}_2 \longrightarrow 2\text{Na}_2\text{CO}_3 + \text{O}_2$

Thus, (c)

21. (c)

22. (a) (s-block)

(b) (p-block)

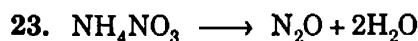
(c)  $1s^2 2s^2$  in ground state — (s-block) and  $1s^2 2s^1 2p^1$  in excited state.

(d)  $[\text{Ar}] 4s^2$  — ground state

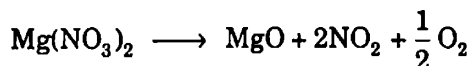
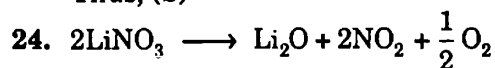
$[\text{Ar}] 4s^1 4p^1$  — excited state

Thus, s-block.

Thus, (b)



Thus, (b)

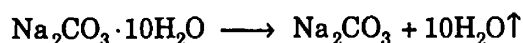


Thus, (c)

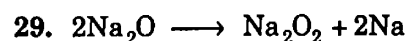
25. (d)    26. (d)

27. Mg does not react with NaOH.

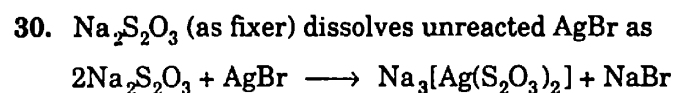
Thus, (c)



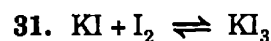
Thus, (c)



Thus, (b)



Thus, (c)



Thus, (a)

32. Refer Q. 31

Thus, (c)

33. (d)



Thus, (b) is incorrect.

35. (d)    36. (a)    37. (b)

38. Smaller cation polarises anion to a greater extent hence larger covalent nature and thus lattice energy.

Thus, (a)

39. (a)

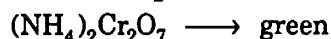
40.  $\text{KO}_2$  ( $\text{O}_2^-$  is paramagnetic due to one unpaired electron)

$\text{NO}_2$  (is paramagnetic due to one unpaired electron on N)

Thus, (a)

41. (a)    42. (c)

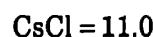
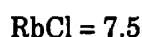
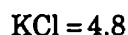
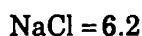
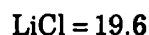
43.  $\text{LiNO}_3$  on ignition imparts crimson red,



Thus, (d)

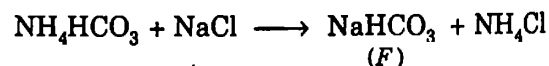
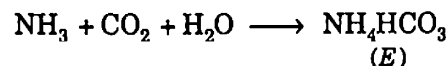
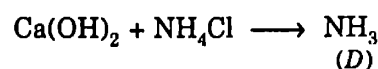
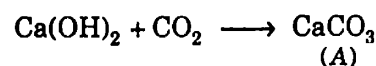
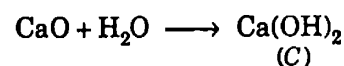
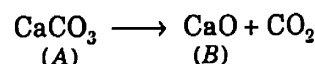
44. (c)

45. Molar solubility is in  $\text{mol L}^{-1}$  (Reference concise inorganic chemistry J.D. Lee)

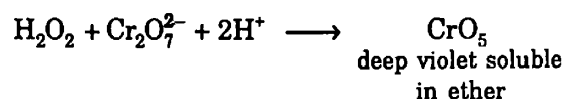
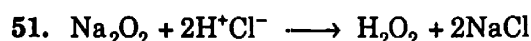


Thus, (c)

### Solution 46-50



46. (a)    47. (b)    48. (a)    49. (b)    50. (a)



Thus, (a)

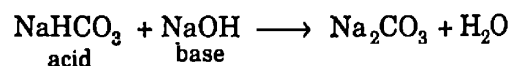
52.  $(\text{CaCN}_2 + \text{C})$

Thus, (b)

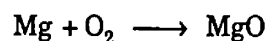
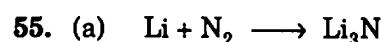
53. Potassium antimonyl tartrate

Thus, (b)

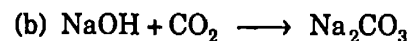
54.  $\text{NaHCO}_3$  is acidic and decomposed by NaOH forming  $\text{Na}_2\text{CO}_3$



Thus, (c)



$\text{O}_2$  and  $\text{N}_2$  are removed



$\text{CO}_2$  is removed

Thus, (c)

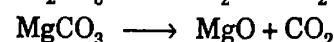
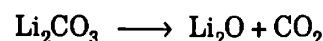
56. (c)

57. HCHO is used as preservatives of dead biological specimen.

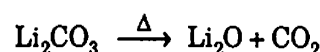
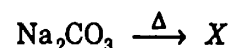
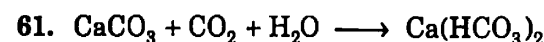
Thus, (d)

58. (c)    59. (b)

60.  $\text{Li}_2\text{CO}_3$  and  $\text{MgCO}_3$  are decomposed by heating



Thus, (c)



$\text{CaCl}_2/\text{CaSO}_4$  make permanent hardness.

Thus, (a)

62.  $\text{Na}^+$  is alkalide ion

$\text{Na}(1s^2 2s^2 2p^6 4s^1) \leftarrow$  Paramagnetic due to unpaired electrons

$\text{Na}^+(1s^2 2s^2 2p^6 3s^2) \leftarrow$  diamagnetic due to paired electrons

Thus, (a)

63. (d) 64. (d) 65. (b)

66. Smaller cation, larger hydration thus smaller molar ionic conductance

Ionic size  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+$

Hydration  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$

Size of hydration ion  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$

Molar ionic conductance  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+$

Thus, (a)

67. (a) 68. (b)

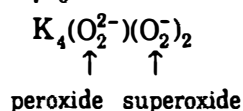
69.  $\text{M}_2\text{O}_3$  actually exists as  $\text{M}_4\text{O}_6 [\text{M}_4(\text{O}_2^{2-})(\text{O}_2^-)_2]$

$\text{O}_2^-$  is paramagnetic.

Thus, (b)

70.  $\text{KO}_2$  is paramagnetic due to  $\text{O}_2^-$

$\text{K}_2\text{O}_3$  is actually  $\text{K}_4\text{O}_6$



Thus, it also paramagnetic.

Thus, (c)

71. (d) 72. (b) 73. (a) 74. (d) 75. (c)

### One or More Than One Options Correct

1. (a), (b), (c), (d) 2. (a), (b) 3. (a), (b)  
4. (a), (c), (d) 5. (a), (b) 6. (b), (c) 7. (a), (b), (d)  
8. (a), (d) 9. (b), (c), (d) 10. (a), (b), (c) 11. (a)  
12. (a), (b), (c) 13. (a), (b), (c) 14. (a), (b), (c)  
15. (a), (b), (c)

### Passage Comprehension Questions

#### Passage 1

1. (b) 2. (c)

#### Passage 2

1. (a)  $\Delta H_{\text{(Hydration)}} = \Delta H_{\text{hydration}}(\text{cation}) + \Delta H_{\text{hydration}}(\text{anion})$   
2. (d)

3. (c)  $\Delta H_{\text{solution}} = \Delta H_{\text{hydration}} - \Delta H_U$

$$\Delta H_{\text{solution}}(\text{LiCl}) = -499 - 382 + 840 \\ = -41 \text{ kJ mol}^{-1}$$

$$\text{NaCl} = -4 \text{ kJ mol}^{-1}$$

$$\text{KCl} = +16 \text{ kJ mol}^{-1}$$

4. (a)

#### Passage 3

1. (b) 2. (c) 3. (c) 4. (a), (c)

#### Passage 4

1. (b) 2. (a) 3. (d) 4. (b)

$$5. (c) w = zit = \frac{40 \times 1.08 \times 137}{96500 \times 1} = 0.06 \text{ g}$$

$$6. (b) 0.06 \text{ g NaOH per } 0.0445 \text{ L,} \\ \text{Conc. in mol L}^{-1} = \frac{0.06}{40 \times 0.0445} = 3.37 \times 10^{-3} \text{ M}$$

$$\therefore [\text{OH}^-] = 3.37 \times 10^{-3} \text{ M}$$

$$p_{\text{OH}} = 2.47$$

$$p_{\text{H}} = 11.53$$

#### Passage 5

1. (a) 2. (a) 3. (c) 4. (b)

#### Passage 6

1. (b) 2. (a) 3. (b)

#### Passage 7

1. (a) 2. (c) 3. (a)

#### Passage 8

1. (a) 2. (b) 3. (c) 4. (d)

### Assertion & Reason

1. (a) 2. (a) 3. (b) 4. (b) 5. (a) 6. (a)  
7. (a) 8. (b) 9. (a) 10. (a) 11. (c) 12. (d)  
13. (a) 14. (c) 15. (b) 16. (c)

### True & False

1. F, ( $\text{KO}_2$  is paramagnetic) 2. T 3. T  
4. F:  $\text{Li}_2\text{CO}_3$  is decomposes into  $\text{CO}_2$  and  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3$  does not  
5. F,  $\text{Na}_2\text{CO}_3$  is not decomposed on heating.  
6. T 7. T 8. T 9. T  
10. F: Ionic hydride 11. T 12. T  
13. F: Na formed reacts with  $\text{H}_2\text{O}$  giving  $\text{NaOH}$  and  $\text{H}_2$ .  
14. T  
15. F: Smaller size of  $\text{Li}^+$  cannot set into double salt.  
16. T 17. F:  $\text{KHCO}_3$  is more soluble.  
18. T 19. T 20. T

### Fill in the Blanks

1. Li, Mg 2.  $\text{KO}_2$  3. Zn/Al/Be 4.  $\text{NaHCO}_3$   
5. standard reduction electrode potential  
6. smaller size, greater charge density, lack of d-orbital  
7. blue, blue, solvated 8. Li 9.  $\text{Li}_2\text{CO}_3$

3. (a) E and G (b) C, E, and G (c) G (d) A and D  
(e) B

# s-Block Elements

## —The Alkaline Earth Metals

Group 2 family members (alkaline-earth elements) are not free from tension. The youngest of the family (Be) and the younger one (Mg) does not have patch with other members. Be has tied up with Al (Group 13) and Mg with Li (Group 1) — a diagonal relationship. “Ghar ka Bhedi Lanka Dhaye.”

- General electronic configuration is [Inert gas]  $ns^2$  — Alkaline earth metals; Group 2(IIA)  $n$  signifies period and number of valence electrons in  $ns$ , its group.

Alkaline Earth Metals

| Iron             | EC                   | Z  | 2(IIA) |
|------------------|----------------------|----|--------|
| Be <sup>2+</sup> | [He] 2s <sup>2</sup> | 4  | Be     |
| Mg <sup>2+</sup> | [Ne] 3s <sup>2</sup> | 12 | Mg     |
| Ca <sup>2+</sup> | [Ar] 4s <sup>2</sup> | 20 | Ca     |
| Sr <sup>2+</sup> | [Kr] 5s <sup>2</sup> | 38 | Sr     |
| Ba <sup>2+</sup> | [Xe] 6s <sup>2</sup> | 56 | Ba     |
| Ra <sup>2+</sup> | [Ra] 7s <sup>2</sup> | 88 | Ra     |

**Alkali earth metals** form compounds with +2 oxidation state ions, having nearest stable noble gas configuration.

- Magnesium is an important constituent of chlorophyll which initiates the process of photosynthesis in green plants.
- Magnesium ion are concentrated more in intracellular than in extracellular fluids in animal bodies. Their presence is also necessary for the activation of phosphate-transfer enzymes. These enzymes take part in the biochemical process (exothermic) occurring in animal body. Mg<sup>2+</sup> ions are also involved in carbohydrate metabolism.
- Ca<sup>2+</sup> ions are essential for the formation of bones and teeth. The enamel on teeth is a double salt  $3Ca_3(PO_4)_2 \cdot CaF_2$ .
- Mg<sup>2+</sup> and Ca<sup>2+</sup> ions are also involved in the transmission of electrical impulses along the nerve fibre and for the contraction of muscles.

### Learning Framework of the Chapter

- Periodicity at a Glance
- Reactions of Alkaline Earth Metals
- Compounds of Alkaline Earth Metals
- Anomalous Behaviour of Beryllium
- Additional Reactions and Facts
- Alkaline Earth Metal Compounds

|                  |                  |
|------------------|------------------|
| <sup>1</sup> H   |                  |
| <sub>3</sub> Li  | <sub>4</sub> Be  |
| <sub>11</sub> Na | <sub>12</sub> Mg |
| <sub>19</sub> K  | <sub>20</sub> Ca |
| <sub>37</sub> Rb | <sub>38</sub> Sr |
| <sub>55</sub> Cs | <sub>56</sub> Ba |
| <sub>87</sub> Fr | <sub>88</sub> Ra |



## Periodicity at a Glance

Detailed periodicity has been given in chapter 3. Periodicity of s-block elements is summarised below.

There is uniform gradation in properties except in case of Li and Be which being smallest in their groups show abnormal behaviour. Li resembles Mg and Be resembles Al that we call **diagonal relationship**.

### Periodicity in s-Block Elements

- A** : Atomic number  
**B** : Effective nuclear charge ( $Z^* = Z - \sigma$ )  
 where  $\sigma$  is screening constant  
**C** : Number of shells  
**D** : Atomic radius  
**E** : Ionisation energy  
**F** : Hydration and hydration energy  
**G** : Size of hydrated ion  
**H** : Polarising power (based on Fajan's rule)  
**I** : Lattice energy of chloride  
**J** : Reactivity  
**K** : Ionic conductance

- From the above table, it is concluded that due to higher (IE) of alkaline earth metals, they are less reactive than alkali metals.

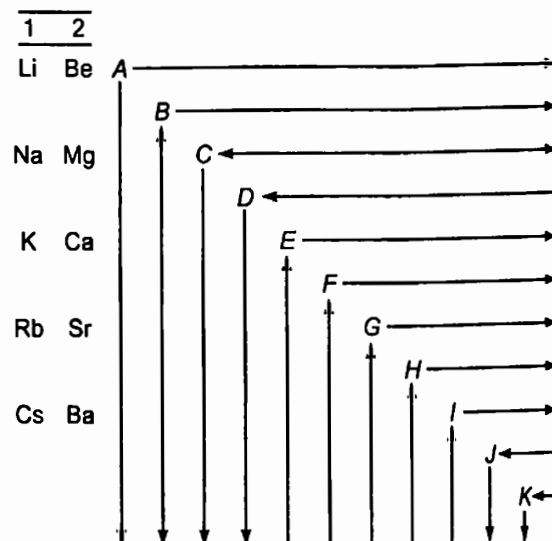


Table 9.1 Summarises some of the properties of alkaline earth metals [Group 2(IIA)]

Table 9.1 Properties of the Alkaline Earth Metals

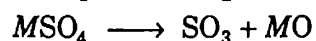
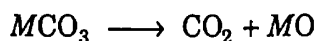
| Properties                                                                                                             | Be                     | Mg                   | Ca                   | Sr                   | Ba                   | Ra                   |
|------------------------------------------------------------------------------------------------------------------------|------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Atomic number                                                                                                          | 4                      | 12                   | 20                   | 38                   | 56                   | 88                   |
| Atomic mass                                                                                                            | 9.012                  | 24.3050              | 40.078               | 87.62                | 137.327              | 226.0254             |
| Effective nuclear charge                                                                                               | 1.95                   | 2.85                 | 2.85                 | 2.85                 | 2.85                 | 2.85                 |
| Ground state electron configuration                                                                                    | [He] 2s <sup>2</sup>   | [Ne] 3s <sup>2</sup> | [Ar] 4s <sup>2</sup> | [Kr] 5s <sup>2</sup> | [Xe] 6s <sup>2</sup> | [Rn] 7s <sup>2</sup> |
| Metallic radius, (pm)                                                                                                  | 112                    | 160                  | 197                  | 215                  | 222                  | —                    |
| Ionic radius, (pm)                                                                                                     | 31                     | 72                   | 100                  | 118                  | 135                  | —                    |
| Ionic charge density<br>(ionic charge/radius (Å))                                                                      | 6.45                   | 2.78                 | 2.00                 | 1.69                 | 1.48                 | —                    |
| (IE) <sub>1</sub> , kJ mol <sup>-1</sup>                                                                               | 899                    | 737                  | 590                  | 549                  | 503                  | 508                  |
| (IE) <sub>2</sub> , kJ mol <sup>-1</sup>                                                                               | 1757                   | 1450                 | 1145                 | 1064                 | 965                  | 975                  |
| [(IE) <sub>1</sub> + (IE) <sub>2</sub> ] kJ mol <sup>-1</sup>                                                          | 2656                   | 2187                 | 1735                 | 1613                 | 1468                 | 1483                 |
| (IE) <sub>3</sub> , (kJ mol <sup>-1</sup> )                                                                            | 14850                  | 7730                 | 4940                 | 4150                 | 3440                 | —                    |
| Pauling's electronegativity                                                                                            | 1.5                    | 1.2                  | 1.0                  | 1.0                  | 0.9                  | —                    |
| $\Delta H^\circ_{\text{hydr}}$ , Hydration energy, kJ mol <sup>-1</sup><br>$M^{2+}(g) + aq \longrightarrow M^{2+}(aq)$ | -2494                  | -1921                | -1577                | -1443                | -1305                | —                    |
| $\Delta S^\circ_{\text{hydra}}$ of $M^{2+}$ / JK <sup>-1</sup> mol <sup>-1</sup>                                       | -300                   | -320                 | -230                 | -220                 | -200                 | —                    |
| $\Delta G^\circ_{\text{hydra}}$ of $M^{2+}$ / kJ mol <sup>-1</sup>                                                     | -2410                  | -1845                | -1525                | -1400                | -1265                | —                    |
| $\Delta H^\circ_{\text{atoms}}$ / kJ mol <sup>-1</sup>                                                                 | 326                    | 149                  | 177                  | 164                  | 178                  | 130                  |
| Density at 25°C (g cm <sup>-3</sup> )                                                                                  | 1.848                  | 1.738                | 1.55                 | 2.54                 | 3.51                 | 5                    |
| Colour                                                                                                                 | Grey                   | Silver               | Silver               | Silver               | Silver-yellow        | Silver               |
| Enthalpy of fusion $\Delta H^\circ_{\text{fusion}}$ / kJ mol <sup>-1</sup>                                             | 11.6                   | 8.95                 | 8.95                 | 9.62                 | 7.66                 | 7.25                 |
| Bond enthalpy of $M_2$ (kJ mol <sup>-1</sup> )                                                                         | 9.46                   | —                    | —                    | —                    | —                    | —                    |
| Electrode potential, $E^\circ$ , (V)<br>$M^{2+}(aq) + 2e^- \longrightarrow M(s)$                                       | -1.85                  | -2.37                | -2.87                | -2.89                | -2.90                | -2.92                |
| Melting point/°C                                                                                                       | 1287                   | 649                  | 839                  | 768                  | 727                  | 700                  |
| Boiling point/°C                                                                                                       | 2500                   | 1105                 | 1494                 | 1381                 | 1850                 | 1140                 |
| Abundance on earth %                                                                                                   | 2.8 × 10 <sup>-3</sup> | 2.33                 | 4.15                 | 0.038                | 0.042                | trace                |

- Like the alkali metals they also form predominantly ionic compounds but tendency towards covalency is greater, particularly with Be and Mg because of their smaller atomic and ionic radii.
- Be forms compounds which are essentially covalent.
- Alkaline earth metal ions, because of their larger charge to size ratio, exert a much stronger electrostatic attraction on the oxygen of water molecules surrounding them.
- Since the alkaline earth metals (except Be) tend to lose their valence electrons readily, they act as strong reducing agents as indicated by  $E_{\text{red}}^{\circ}$  values. (Table 9.1). The particularly less negative value for Be arises from the large hydration energy associated with the small size of  $\text{Be}^{2+}$  and the relatively large value of heat of sublimation.
- Basic nature of oxides increases down the group but solubilities of sulphates and carbonates decrease as ionic size increases.

### Thermal Stability of Oxy Salts

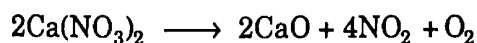
All the group 2 elements form oxysalts. The thermal stability of the oxysalts increases with the increase in electropositivity of the metals. Thus it increases down the group. The thermal stability of the salts of group 2 is less than those of the group 1 metals.

- The sulphates are stable to heat whereas the carbonates decompose to give MO and  $\text{CO}_2$ , the temperature of decomposition increasing from Mg to Ba.  $\text{BeCO}_3$  is kept in the atmosphere of  $\text{CO}_2$  to prevent its decomposition.



|                 |                 |                 |                 |                 |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| $\text{BeCO}_3$ | $\text{MgCO}_3$ | $\text{CaCO}_3$ | $\text{SrCO}_3$ | $\text{BaCO}_3$ |
| < 100°C         | 540°C           | 900°C           | 1290°C          | 1360°C          |
| $\text{BeSO}_4$ | $\text{MgSO}_4$ | $\text{CaSO}_4$ | $\text{SrSO}_4$ | —               |
| 575°C           | 875°C           | 1100°C          | 1375°C          | —               |

Alkali metal nitrates decomposes into nitrites on heating whereas alkaline earth metal nitrates decompose on heating to metal oxide, nitrogen dioxide and oxygen.



### DEEP Focus

#### Atomic and Ionic Radii

The atoms of the alkaline earth metals are smaller than those of the corresponding group 1 elements. This is because of the increase in effective nuclear charge with increase in atomic number. Due to increase in effective nuclear charge, valence shell electrons are pulled in more firmly by the nucleus, thereby reducing the size of the atoms. Similarly, their ionic radii are also smaller than those of group 1 elements, because the removal of two orbital electrons increase the effective nuclear charge even further.

The atomic and ionic radii increase from Be to Ra due to the effect of extra shells of electrons being added. This outweighs the effect of increased nuclear charge.

These elements are denser than group 1 metals because they have two valence electrons per atom for bonding the atoms into a metallic lattice and as a result more mass can be packed into a smaller volume. The density decreases slightly on moving down the group from Be to Ca but increases considerably there after up to Ra.

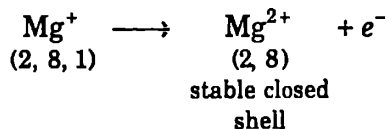
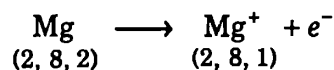
### Melting Point

Group 2 metals have higher melting points when compared to the group 1 metals. The reason being +2 charge on the cations in the metallic lattice, causing them to be more strongly attracted to the 'sea of electrons' and making it difficult to pull them apart.

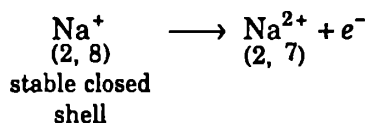
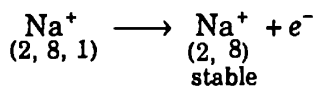
### Ionisation Energy

The first ionisation energy (Table 9.1) of alkaline earth metals is more than that of corresponding alkali metals. This is because the alkaline earth metals have higher effective nuclear charge and are smaller in size, thereby the electrons are more tightly held to the nucleus. The second ionisation energy of these elements is almost twice first ionisation energy. This is because once one electron has been removed, the effective nuclear charge felt by orbital electrons is increased, so that the remaining electrons are more tightly held and hence, much more energy is needed to remove the second electron. However, their second ionisation energy is less than that of the corresponding alkali metals because of stability of a closed shell configuration of the univalent cations that are formed in the latter cases. The ionisation energy of alkaline earth metals also decreases on moving down the group.

Lower second ionisation energies of the alkaline earth metals as compared to those of alkali metals can be exemplified below :



(Electronic  
configuration of  
the metal and the  
ion is given in  
brackets)



Electropositive character and the reducing property (tendency to lose electrons) increase on moving down the group.

As the alkaline earth metals may lose electrons quite easily, they form divalent cations which have a noble gas structure with no unpaired electrons. Therefore, their compounds are diamagnetic and colourless, unless the anion is coloured. Ca, Sr and Ba compounds give characteristic flame colourations which are used to identify them —

| Ion              | Colour      |
|------------------|-------------|
| $\text{Ca}^{2+}$ | Brick-red   |
| $\text{Sr}^{2+}$ | Crimson     |
| $\text{Ba}^{2+}$ | Apple-green |
| $\text{Ra}^{2+}$ | Carmine-red |

## Solubility, Lattice Energy and Hydration Energy

The metal ions are easily hydrated, *e.g.*,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ . The hydration energies of these ions are much greater than those of alkali metal ions (Table 9.2), because of their smaller size and increased cationic charge. The lattice energies (Table 9.2) of alkaline earth metal salts are also much higher than those of alkali metal salts.

### DEEP Focus

Hydration and lattice energies decrease with increase in size of metal ions. Decreasing lattice energy favours increased solubility, whilst decreasing hydration energy favours decreased solubility. If on moving down a group the hydration energy decreases more rapidly than the lattice energy, the compound becomes less soluble.

This occurs with most of the compounds except for fluorides and hydroxides for example, solubility of sulphates decreases from  $\text{BeSO}_4$  to  $\text{BaSO}_4$ . Due to their small ionic radii,  $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$  have high hydration energies. Thereby  $\text{BeSO}_4$  and  $\text{MgSO}_4$  are soluble in water.  $\text{CaSO}_4$  is only slightly soluble in water, whereas  $\text{SrSO}_4$  and  $\text{BaSO}_4$  are almost insoluble in water. This solubility of sulphates is in order :



### DEEP Focus

In case of fluorides and hydroxides, the lattice energy decreases more rapidly than their hydration energy. This causes a reverse trend, *i.e.*, the fluorides and hydroxides increases in solubility on moving down the group. Thus, order of solubility is

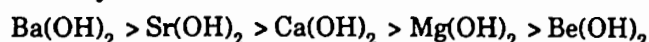


Table 9.2 Enthalpies of Hydration,  $\Delta H_{\text{hyd}}$ , of Alkaline Earth Metal Ions,  $M^{2+}$  and Lattice Energies,  $\Delta H_{\text{latt}}$ , of their Oxides, Carbonates Fluorides and Iodides in  $\text{kJ mol}^{-1}$

| Element | $\Delta H_{\text{hyd}}$ |       | $\Delta H_{\text{latt}}$ |               |               |
|---------|-------------------------|-------|--------------------------|---------------|---------------|
|         | $M^{2+}$                | MO    | $\text{MCO}_3$           | $\text{MF}_2$ | $\text{MI}_2$ |
| Be      | -2494                   | —     | —                        | —             | —             |
| Mg      | -1921                   | -3923 | -3178                    | -2906         | -2292         |
| Ca      | -1577                   | -3517 | -2986                    | -2610         | -2058         |
| Sr      | -1443                   | -3312 | -2718                    | -2459         | —             |
| Ba      | -1305                   | -3120 | -2614                    | -2367         | —             |

Table 9.3 Occurrence and Uses of Alkaline Earth Metals

| Element   | Abundance                                                 | Main mineral                                                                                                                                                              | Uses                                                                                                                           |
|-----------|-----------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|
| Beryllium | $2.8 \times 10^{-3}\%$                                    | First detected in 1798 in the gemstone beryl and emerald ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ ).                                                            | Used in the corrosion resistant alloys                                                                                         |
| Magnesium | 2.33%, seventh most abundant element in the earth's crust | Pure Mg first prepared in 1808, named after the Thessaly, Greece where large deposits of the mineral are found.                                                           | When alloyed with Al, Mg is widely used as structural material because of its high strength, low density and ease of machining |
| Calcium   | 4.15%, fifth most abundant element in the earth's crust   | $\text{CaCO}_3$ , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum), obtained in pure form in 1808, calcium is derived from the Latin word <i>calx</i> , meaning "lime". | As an alloying agent to harden aluminium, calcium is the primary constituent of teeth and bones                                |
| Strontium | 0.038%                                                    | Discovered in 1787 and named after the small town of Strontian (Scotland)                                                                                                 | $\text{SrCO}_3$ is used for the manufacture of glass for colour TV picture tubes                                               |
| Barium    | 0.042%                                                    | Found in the minerals witherite ( $\text{BaCO}_3$ ) and barite ( $\text{BaSO}_4$ ) after which it is named.                                                               | $\text{BaSO}_4$ is used in medicine as a contrast medium for stomach and intestinal X-rays                                     |
| Radium    | traces                                                    | Isolated as chloride in 1898 from the mineral pitchblende                                                                                                                 | Used in cancer radiotherapy                                                                                                    |

## Group IIA (Alkaline Earth Metals) and Group IIB (Zn, Cd, Hg)

Mg acts as a bridge element between IIA (2) and IIB(12):

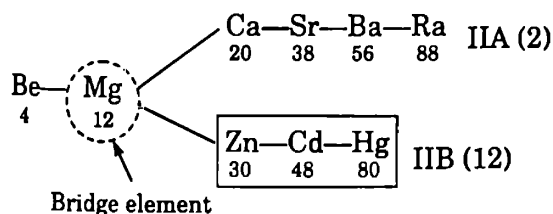


Table 9.4 Distinction Between IIA(2) and IIB(12) Elements

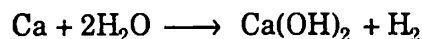
| Properties                 | IIA<br>(Be, Mg, Ca, Sr, Ba, Ra)                                                                               | IIB<br>(Zn, Cd, Hg)                                                 |
|----------------------------|---------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------|
| 1 Electronic configuration | [Inert gas] $ns^2$                                                                                            | [Inert gas] $(n-1)d^{10} ns^2$                                      |
| 2 Block                    | s-block                                                                                                       | d-block                                                             |
| 3 Oxidation state          | +2                                                                                                            | +2, mercury also forms dimeric $Hg_2^{2+}$                          |
| 4 Nature of oxide          | BeO is amphoteric, other oxides are basic<br>$MgO < CaO < SrO < BaO < RaO$                                    | ZnO is amphoteric, CdO and HgO are basic.                           |
| 5 Nature of halides        | Electron-deficient $BeX_2$ are covalent, others ( $MX_2$ ) are ionic:<br>$MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$  | $ZnCl_2, CdCl_2$ are ionic but less than IIA, $HgCl_2$ is covalent. |
| 6 Nature of sulphates      | Less soluble in water and solubility decreases down the group<br>$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$ | more soluble than IIA.                                              |
| 7 Nature of hydroxides     | Solubility of hydroxides increases as we move down the group                                                  | Solubility of hydroxides decreases as we move down the group.       |
| 8 Nature of sulphides      | Soluble                                                                                                       | $ZnS, CdS, HgS$ insoluble and precipitate in salt analysis.         |
| 9 Reactivity               | Increases as we move down the group<br>$Be < Mg < Ca < Sr < Ba$                                               | Decreases as we move down the group<br>$Zn > Cd > Hg$               |

Table 9.5 Reactions of Group 2 (IIA)

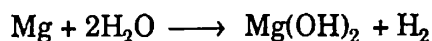
| Reaction                                                                               | Comment                                                                                                                                                                    |
|----------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $M + 2H_2O \longrightarrow M(OH)_2 + H_2$                                              | Be probably reacts with steam, Mg with hot water, and Ca, Sr and Ba react rapidly with cold water.                                                                         |
| $M + 2HCl \longrightarrow MCl_2 + H_2$                                                 | All the metals react with acids liberating $H_2$ . With $HNO_3$ , Be becomes passive due to formation of oxide layer.                                                      |
| $3M + N_2 \longrightarrow M_3N_2$<br>$M_3N_2 + 6H_2O \longrightarrow 2NH_3 + 3M(OH)_2$ | All form nitrides at high temperatures. Stability $Be > Mg > Ca$ (hydrolysis to $NH_3$ ).                                                                                  |
| $M + X_2 \longrightarrow MX_2$<br>( $X_2 = F_2, Cl_2, Br_2, I_2$ )                     | All the metals form $MX_2$ . No polyhalides are formed. (except $BeX_2$ )                                                                                                  |
| $M + 2NH_3 \longrightarrow M(NH_2)_2 + H_2$                                            | All the metals dissolve in liquid $NH_3$ to give deep blue black solutions from which ammoniates $[M(NH_3)_6]^{2+}$ can be recovered and form amides at high temperatures. |
| $2M + O_2 \longrightarrow 2MO$<br>$Ba + O_2 \longrightarrow BaO_2$                     | All the metals form normal oxide. Ba also forms peroxide ( $BaO_2$ ).                                                                                                      |
| $M + H_2 \longrightarrow MH_2$                                                         | Ionic salt-like hydrides formed at high temperatures by Ca, Sr and Ba. Be forms electron-deficient hydrides.                                                               |
| $Be + 2H_2O + 2OH^- \longrightarrow [Be(OH)_4]^{2-} + H_2(g)$                          | Not with other alkaline earth metals.                                                                                                                                      |
| $M(s) + 2C(s) \longrightarrow MC_2(s)$                                                 | At high temperature Be forms $Be_2C$ , ionic compounds.                                                                                                                    |
| $M + S \longrightarrow MS(s)$                                                          | The sulphides are soluble, but hydrolyse if heated in water.                                                                                                               |

## With Water

- Ca, Sr and Ba have reduction potentials ( $E^\circ$ ) similar to those of the corresponding alkali metal and are quite high in the electrochemical series. They react with cold water quite readily.



- Mg has an intermediate value and it does not react with cold water but it decomposes hot water.

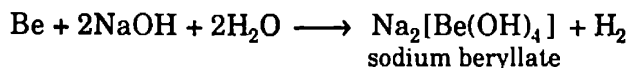


Mg forms a protective layer of oxide, so despite its favourable reduction potential, it does not react readily unless the oxide layer is removed by amalgamating with mercury. In the formation of the oxide film, it resembles aluminium.

- Be is amphoteric, as it reacts with acid as well as with base.

## Reactions of Alkaline Earth Metals

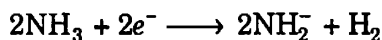
Table 9.5 summarises reactions of group 2 (IIA). From this, it is evident that as we go down the group, reactivity increases.



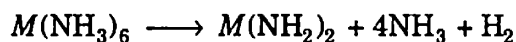
Mg, Ca, Sr and Ba do not react with NaOH and thus are purely basic.

## With Ammonia

- All the metals dissolve in liquid ammonia as do the alkali metals. Dilute solutions are **bright blue** in colour due to the spectrum from the solvated electrons. These solutions decompose very slowly, forming amide and  $\text{H}_2$ , but the reaction is accelerated by many transition metals and their compounds.



Evaporation of the ammonia from solutions of alkali metals yields the metal, but in case of alkaline earth metals, evaporation of ammonia gives hexamminates of the metals, which slowly decompose to give amides:

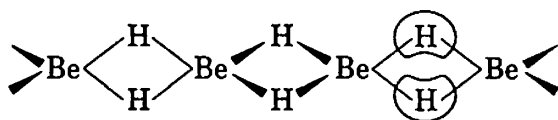


**Concentrated solutions of the metals in ammonia are bronze coloured, due to the formation of metal clusters.**

## DEEP Focus

### Formation of Hydrides

All the group 2 element except beryllium form hydrides,  $\text{MH}_2$ , by direct combination with hydrogen. Beryllium hydride can be formed by reducing beryllium chloride with lithium aluminium hydride,  $\text{LiAlH}_4$ . All these hydrides are reducing agents which react with water and liberate hydrogen. Calcium, strontium and barium hydrides are ionic and contain the hydride ion,  $\text{H}^-$ . Beryllium and magnesium hydrides are covalent and polymeric.  $(\text{BeH}_2)_n$  has an interesting structure. The polymeric solid contains hydrogen bridges between beryllium atoms.



Beryllium hydride polymer

Each beryllium atom is bonded to four hydrogen atoms and each hydrogen atom forms two bonds as it is bridging two Be atoms. Since Be has two valence electrons and H only one, it is apparent that there are not enough electrons to form the usual electron pair bonds in which two electrons are shared between two atoms. Instead of this, **three-centre bonds are formed in which a 'banana-shaped' molecular orbital covers three atoms  $\text{Be} \dots \text{H} \dots \text{Be}$ , and contains two electrons.** The monomeric molecule  $\text{BeH}_2$ , if formed with normal bonds, would have only four electrons in the outer shell of the beryllium atom and would be electron deficient.

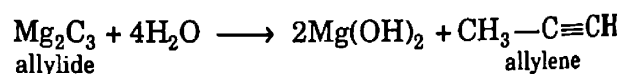
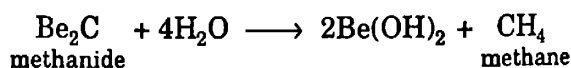
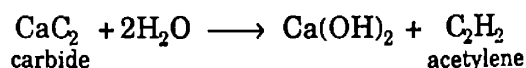
**This would make the molecule very unstable; that is why  $\text{BeH}_2$  exists as a polymer.** This is an example of a cluster compound in which each atom shares

its electrons with several neighbours and receives a share in their electrons to acquire a stable configuration.

## Formation of Carbides

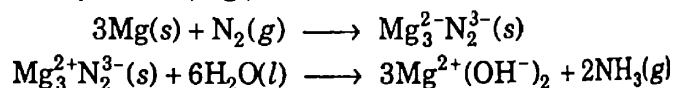
All the metals in the Mg-Ba series of their oxides react directly with carbon to give the carbides (acetylides),  $\text{MC}_2$ . These carbides are ionic in nature and have a NaCl type of structure with  $\text{M}^{2+}$  replacing  $\text{Na}^+$  and  $\text{C} \equiv \text{C}^{2-}$  replacing  $\text{Cl}^-$ . Beryllium forms **methanide**,  $\text{Be}_2\text{C}$ , with carbon and acetylide,  $\text{BeC}_2$ , with acetylene. Magnesium on heating with carbon forms  $\text{Mg}_2\text{C}_3$  also, which is an allylide since with water it liberates **allylene (methylacetylene)**.

The carbides are named depending upon the hydrocarbon they liberate on reaction with water. If it liberates acetylene, it will be named acetylide, and if methane is liberated, it will be called as '**methanide**', etc.



## Formation of Nitrides

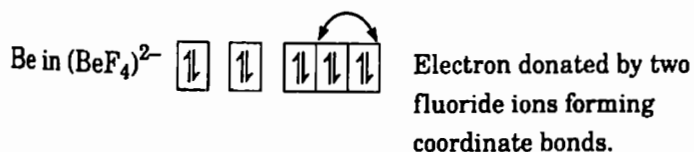
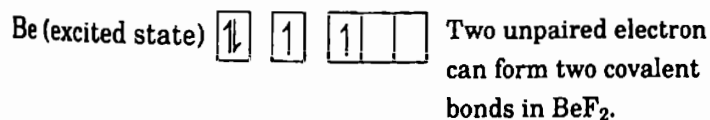
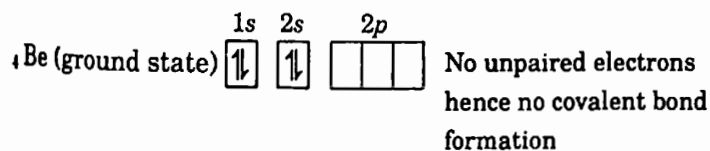
The alkaline earth metals burn in **nitrogen and form nitrides,  $\text{M}_3\text{N}_2$** . It requires a lot of energy to convert the stable  $\text{N}_2$  molecule into nitride ion,  $\text{N}^{3-}$ , and this is recovered from the very high lattice energies of the alkaline earth metal nitrides. The beryllium compound is rather volatile while others are not. They are all colourless crystalline solids which decompose on heating and react with water to liberate ammonia and form either the metal oxide or hydroxide, e.g.,



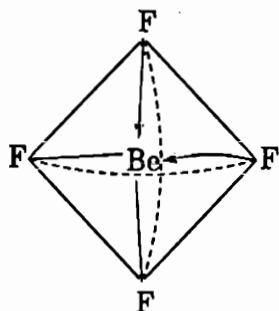
## Complexation Behaviour

Complex formation is favoured by small, highly charged cations with suitable empty orbitals of approximately the right energy with which the ligand orbitals can combine.

Alkaline earth metals form more complexes as compared to alkali metals. The tendency to form complexes (mostly with O and N donors) decreases with increasing atomic number. Thus, of the heavier ions only  $\text{Ca}^{2+}$  forms a complex with ethanol. Beryllium having the smallest ion in the group tends to form complexes most readily. It mostly forms complexes with tetrahedral arrangement because of the available orbitals as shown below :

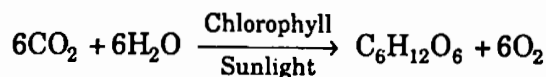


However, once these are formed, all the Be—F bonds  
tend to become similar.

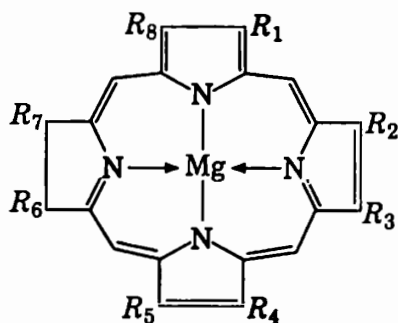


In the hydrated salts, *e.g.*,  $\text{BeCO}_3 \cdot 4\text{H}_2\text{O}$  and  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ , beryllium ions exist in the form  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ , where they show a coordination number of four.

Magnesium is known to form a very important complex occurring in nature, *viz*; chlorophyll; a green pigment of the plants which produces sugar for the plants in presence of sunlight,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in a process called photosynthesis.



Magnesium, in chlorophyll, is coordinated to four nitrogen atom in the heterocyclic porphyrin ring system as shown.



Skeleton of chlorophyll molecule

The rest of the element from calcium to barium form complexes only with strong complexation agents such as acetylacetone, ethylenediamine, terephthalic acid (EDTA), etc. In fact, titrations are performed using EDTA in buffer solutions to estimate the amounts of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  present in water, to determine the hardness of water.

## Target Practice 1

- Out of  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$  and Ca
  - Which has maximum IE? .....
  - Which is maximum hydrated? .....
  - Which has least size? .....
  - Which has maximum size? .....
  - Which is most stable? .....
  - Which is least stable? .....
- $\text{BeCO}_3$  is decomposes easily. Hence, it is kept in the atmosphere of ..... to prevent its decomposition.
- In Group 2 (IIA)
  - Maximum basic oxide is .....
  - Maximum soluble sulphate is .....
  - Maximum soluble carbonate is .....
  - Maximum soluble fluoride is .....
  - Maximum hydrated ion is .....

## Answers

- (a)  $\text{Be}^{2+}$  (b)  $\text{Be}^{2+}$  (c)  $\text{Be}^{2+}$  (d) Ca (e) Ca (f)  $\text{Mg}^{2+}$
- $\text{CO}_2$
- (a)  $\text{RaO}$  (b)  $\text{BeSO}_4$  (c)  $\text{BeCO}_3$  (d)  $\text{RaF}_2$  (e)  $\text{Be}^{2+}$

## Practice Exercise 1

- Arrange the following properties, as indicated, in the increasing order
  - Lattice energy of  $\text{BeCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$
  - Solubility of  $\text{BeSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{CaSO}_4$ ,  $\text{SrSO}_4$ ,  $\text{BaSO}_4$
  - Stability of  $\text{BeCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{CaCO}_3$
  - Stability of  $\text{BeSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{CaSO}_4$
  - Size of the hydrated ions of  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$
  - Solubility of  $\text{Be}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$
  - Covalent nature of  $\text{BeCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$
  - Hydrolysis of  $\text{BeCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$

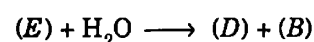
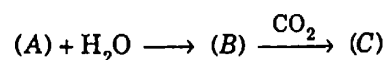
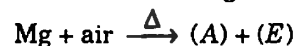
2. Lattice energies of  $\text{BeF}_2$ ,  $\text{MgF}_2$  and  $\text{BaF}_2$  are given in Table 9.2.

Hydration energies of  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{F}^-$  are  $-2494$ ,  $-1921$ ,  $-1305$  and  $-457 \text{ kJ mol}^{-1}$ . Which of the  $\text{BeF}_2$ ,  $\text{MgF}_2$  and  $\text{BaF}_2$  is soluble in water?

3. Arrange the following in increasing order:
- Basic nature of Be, Mg, Ca, Sr
  - Reactivity of BeO, MgO, CaO with  $\text{H}_2\text{O}$
  - Refractory properties of BeO, MgO, CaO
  - Reaction of Li, Mg and Ca with  $\text{N}_2$
  - Reaction of Be, Mg, Ca with  $\text{H}_2\text{O}$

4. What are the possible products when Mg is burnt in air and they are decomposed by  $\text{H}_2\text{O}$ ?

5. Identify (A) to (E) in the following:



$\xrightarrow{\text{HCl}}$  white fumes

1 mole of (B) neutralises 2 moles of HCl.

## Answers

1. (a)  $\text{SrCl}_2 < \text{CaCl}_2 < \text{MgCl}_2 < \text{BeCl}_2$   
 (b)  $\text{BaSO}_4 < \text{SrSO}_4 < \text{CaSO}_4 < \text{MgSO}_4 < \text{BeSO}_4$   
 (c)  $\text{BeCO}_3 < \text{MgCO}_3 < \text{CaCO}_3$   
 (d)  $\text{BeSO}_4 < \text{MgSO}_4 < \text{CaSO}_4$   
 (e)  $\text{Ca}^{2+} < \text{Mg}^{2+} < \text{Be}^{2+}$   
 (f)  $\text{Be}(\text{OH})_2 < \text{Mg}(\text{OH})_2 < \text{Ca}(\text{OH})_2$   
 (g)  $\text{CaCl}_2 < \text{MgCl}_2 < \text{BeCl}_2$   
 (h)  $\text{CaCl}_2 < \text{MgCl}_2 < \text{BeCl}_2$

2. Hydration energy of

$$\text{BeF}_2 = -2494 + 2 \times (-457) = -3408 \text{ kJ mol}^{-1}$$

$$\text{MgF}_2 = -1921 + 2 \times (-457) = -2835 \text{ kJ mol}^{-1}$$

$$\text{BaF}_2 = -1305 + 2 \times (-457) = -2219 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{Solution}} = \Delta H_{\text{Hydration}} - \text{Lattice energy}$$

$$\text{BeF}_2 = -3408 - (-2906) = -502 \text{ kJ mol}^{-1}$$

$$\text{MgF}_2 = -2835 - (-2610) = -225 \text{ kJ mol}^{-1}$$

$$\text{BaF}_2 = -2219 - (-2367) = 148 \text{ kJ mol}^{-1}$$

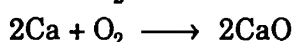
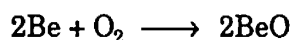
In  $\text{BaF}_2$ ,  $\Delta H_{\text{soln}}$  is +ve hence,  $\text{BaF}_2$  is soluble in water.

3. (a)  $\text{Be} < \text{Mg} < \text{Ca} < \text{Sr}$  (b)  $\text{BeO} < \text{MgO} < \text{CaO}$   
 (c)  $\text{CaO} < \text{MgO} < \text{BeO}$  (d)  $\text{Ca} < \text{Li} < \text{Mg}$  (e)  $\text{Be} < \text{Mg} < \text{Ca}$   
 4.  $\text{MgO}$ ,  $\text{Mg}_3\text{N}_2$  changing to  $\text{Mg}(\text{OH})_2$  and  $\text{NH}_3$ . (also refer Q.5 below)  
 5. (A) :  $\text{MgO}$  (B) :  $\text{Mg}(\text{OH})_2$  (C) :  $\text{MgCO}_3$  (D) :  $\text{NH}_3$   
 (E) :  $\text{Mg}_3\text{N}_2$

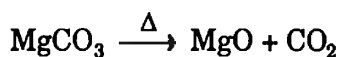
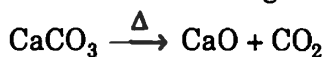
## Compounds of Alkaline Earth Metals

### Oxides and Hydroxides

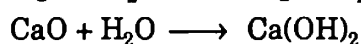
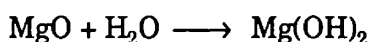
- Oxides are formed either by heating the metals in oxygen:



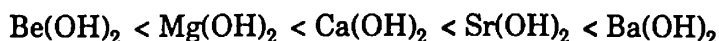
or by heating their carbonates at high temperatures:



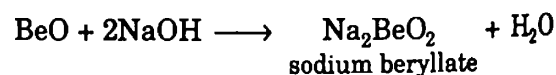
- The oxides are highly stable due to large ionic crystal lattice energies. The values are so high in the case of oxides of Be and Mg that these compounds are almost insoluble in water. BeO is amphoteric and other oxides are basic and yield hydroxides in aqueous solution.



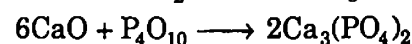
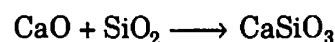
- Basic strength of the hydroxides increases going down the group



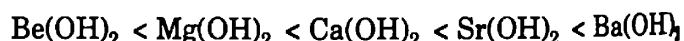
BeO is insoluble in  $\text{H}_2\text{O}$  but dissolves in acid and alkali and is thus amphoteric



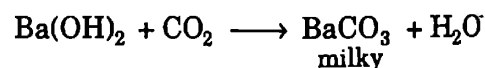
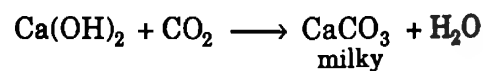
- CaO combines with solid acidic oxides at high temperatures



- MgO is not very reactive, especially if it has been ignited at high temperature and for this reason it is used as a refractory. BeO is also used as a refractory.
- Solubility of hydroxides increases while going down the group



- $\text{Ca}(\text{OH})_2$  is called **lime water** or **slaked lime** and  $\text{Ba}(\text{OH})_2$  is called **baryta water**; lime water or baryta turns milky by  $\text{CO}_2$

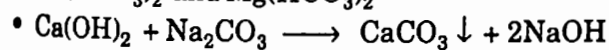


$\text{Ba}(\text{OH})_2$  gives turbidity (milky) even on exhaling breath on it.

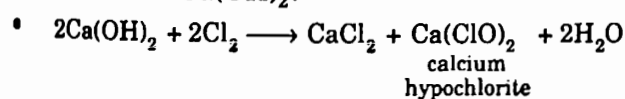
Milky disappears when excess of  $\text{CO}_2$  is passed, due to formation of soluble bicarbonates.



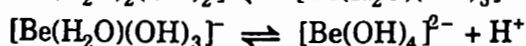
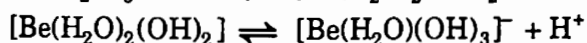
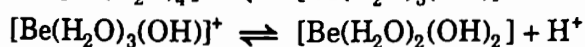
Temporary hardness in water is due to dissolved  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$



This reaction was used in earlier days to manufacture  $\text{NaOH}$  from  $\text{Ca}(\text{OH})_2$ .

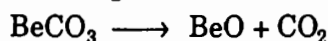


- Solutions of beryllium salts are acidic and dissolve appreciable quantities of  $\text{Be}(\text{OH})_2$ . In alkali solution  $[\text{Be}(\text{OH})_4]^{2-}$  is formed



## Bicarbonates and Carbonates

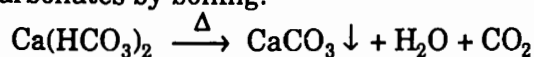
- The carbonates are all ionic, but due to excessive hydration of  $\text{Be}^{2+}$ ,  $\text{BeCO}_3$  is unusual because it contains the hydrated ion  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ .
- $\text{BeCO}_3$  decomposes at low temperature and is placed in the atmosphere of  $\text{CO}_2$



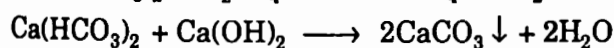
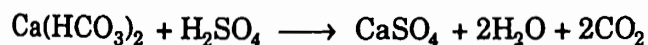
Thermal stability increases with increase in atomic weight down the group or with increasing cationic size.



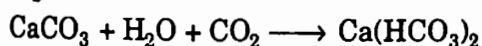
- $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$  exist in water causing temporary hardness which can be removed as insoluble carbonates by boiling:



- $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$  are amphoteric thus neutralised by acid as well as base:



- All of these carbonates are much soluble in a solution of  $\text{CO}_2$  than in water due to formation of bicarbonates



- $\text{SrCO}_3$  is used in the manufacture of glass for colour TV picture tube.

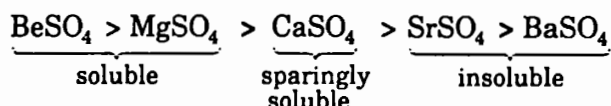
Calcium and barium bicarbonates are stable only in solution and decompose on removal of water to give carbonates. This property of bicarbonates is the reason for **stalactite** and **stalagmite** formation.

**Stalactite** The downward growth of  $\text{CaCO}_3$  formed on the roof of a cave by the trickling of water containing calcium compounds.

**Stalagmite** The upward growth from the floor of a cave; of the same nature and origin as a stalactite.

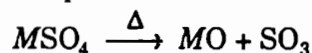
## Sulphates

- The solubility of the sulphates in water decreases down the group.



High solubilities of  $\text{BeSO}_4$  and  $\text{MgSO}_4$  are due to the high enthalpy of hydration of the smaller  $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$  ions, which overcomes the lattice energy factor.

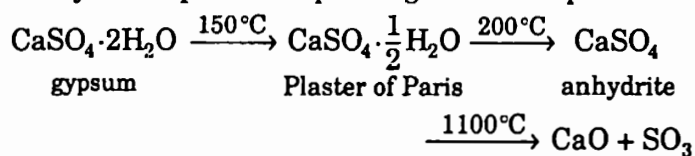
- The sulphates decompose into oxides and  $\text{SO}_3$ .



Thermal stability of the sulphates increases going down the group as shown by decomposition temperatures :

|                 |                 |                 |                 |
|-----------------|-----------------|-----------------|-----------------|
| $\text{BeSO}_4$ | $\text{MgSO}_4$ | $\text{CaSO}_4$ | $\text{SrSO}_4$ |
| 500°C           | 845°C           | 1149°C          | 1374°C          |

- $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  is called Epsom salt and is used as mild laxative. Correct formulation is  $[\text{Mg}(\text{H}_2\text{O})_6] \text{SO}_4 \cdot \text{H}_2\text{O}$  and is isomorphous with zinc sulphate  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ .  $\text{MgSO}_4$  is deliquescent and readily soluble in water. It forms double salts with alkali metal sulphates.  $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  is sold as a fertilizer in the name of 'potash magnesia'.
- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is called gypsum. Heating converts it into variety of compounds depending on the temperature.

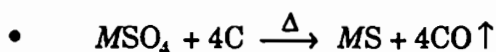


when powdered Plaster of Paris,  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$

( $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$  or  $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$ ) is mixed with stoichiometric amount of water, it sets into a solid mass  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  — gypsum. Plaster of Paris finds use

- for plastering walls
- for making plaster casts (moulds)
- as industrial material
- as sculptural material and
- for encasing limbs so that broken bones are set straight.

- $\text{CaSO}_4 \cdot \text{H}_2\text{O}$  is called Alabaster — a shiny-like marble and is used to make ornaments.

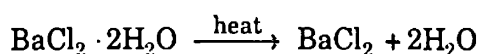




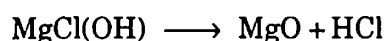
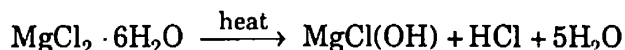
- $\text{BaSO}_4$  is used in medicine as a contrast medium for stomach and intestinal X-rays.

## Halides

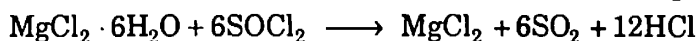
The tendency for the smaller cations to get hydrated is so strong that it is not possible to prepare anhydrous salts by simply heating the hydrated ones. Thus, anhydrous  $\text{BaCl}_2$  may be prepared by heating the hydrated salts beyond  $127^\circ\text{C}$ .



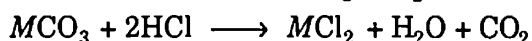
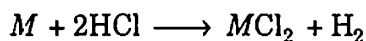
However analogous reaction cannot be carried out for magnesium chloride.



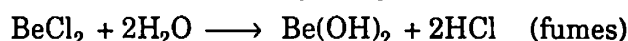
If anhydrous  $\text{MgCl}_2$  is required, it may be obtained by mixing the hydrated salt with thionyl chloride  $\text{SOCl}_2$ .



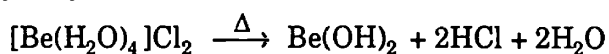
- Halides  $\text{MX}_2$  of alkaline earth metals can be prepared by heating the metals with the halogen acid on either metal or its carbonate :



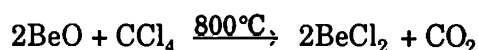
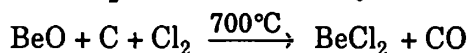
- The beryllium halides are covalent, hygroscopic and fumes in air due to hydrolysis:



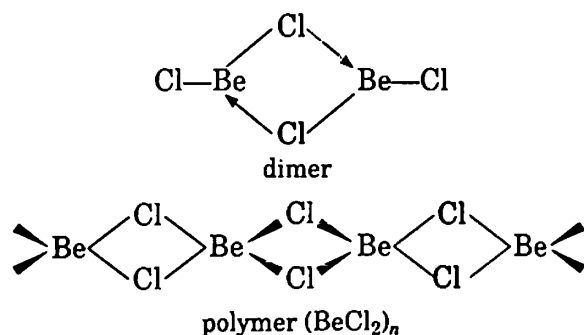
- $\text{BeX}_2$  sublimes on heating and are bad conductor of electricity. In aqueous solution it is difficult to crystallise anhydrous  $\text{BeX}_2$  since dehydration results in hydrolysis:



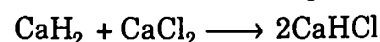
- Anhydrous  $\text{BeX}_2$  can be obtained by :



Anhydrous  $\text{BeCl}_2$  is polymeric. Vapours exist as monomer  $\text{BeCl}_2$  and dimer  $(\text{BeCl}_2)_2$ . Bond length data show that the polymer has three centre two-electron bonds.



- $\text{BeCl}_2$  forms complexes  $\text{M}_2(\text{BeCl}_4)$  with alkali metal chlorides but are decomposed by water.
- $\text{BeF}_2$  is very soluble in water owing to the high solvation energy of  $\text{Be}^{2+}$  in forming  $[\text{Be(H}_2\text{O)}_4]^{2+}$ . The other fluorides  $\text{MF}_2 (\text{M}^{2+} = \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+})$  are all almost insoluble.
- The chlorides, bromides and iodides of Mg, Ca, Sr and Ba are ionic and are readily soluble in water.
- The halides form hydrates and they are hygroscopic.
- $\text{CaCl}_2$  is widely used for treating ice on roads, particularly in very cold countries when it prevents ice formation even up to  $-55^\circ\text{C}$ .
- Mixed chloride hydrides of formula  $\text{MClH}$  which have layer lattices (the different anions occupying different layers) are formed when the hydrides and chlorides of alkaline earth metals are heated together:

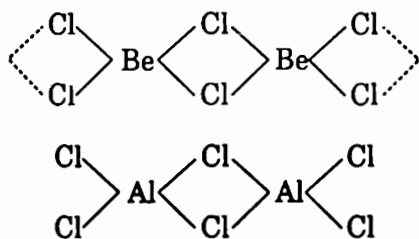


## Anomalous Behaviour of Beryllium

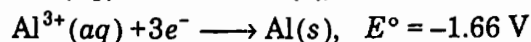
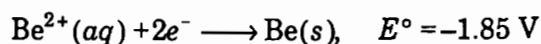
- Because of high (IE) and small atomic size it forms compounds which are largely covalent and its salts are easily hydrolysed.
- $\text{Be} (1s^2 2s^2 2p^0)$  can use only one 2s and three 2p orbital in coordination thus maximum coordination number (CN) of Be is 4 while other elements can show CN of 6 in their compounds by use of d-orbitals in addition to s- and p-orbitals.
- $\text{BeO}$  and  $\text{Be(OH)}_2$  are amphoteric while other oxides are basic.
- The cohesive properties of beryllium are much greater than those of magnesium and other elements in the group. As a result, it is much harder and has higher melting and boiling points.
- Its higher polarising power leads to all its compounds being largely covalent, with lower melting and boiling points and enthalpies of formation. (MP of  $\text{BeF}_2$  is  $800^\circ\text{C}$  that of other fluorides about  $1300^\circ\text{C}$ ). All the compounds of Be are more soluble in organic solvents than the corresponding magnesium compounds. They hydrolyse in water, and in this respect they rather resemble aluminium (diagonal relationship)

## Diagonal Relationship

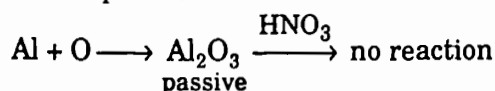
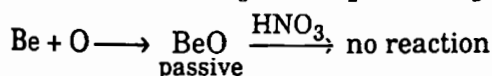
- Beryllium shows a diagonal relationship to aluminium :
  - The chlorides of both Be and Al have bridged structures in vapour phase



- Two metals have similar standard electrode potential:



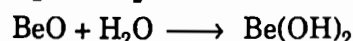
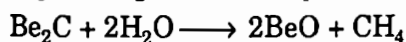
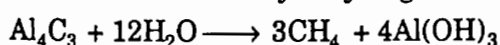
- Both are rendered passive by nitric oxide due to formation of oxide layer



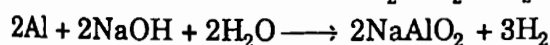
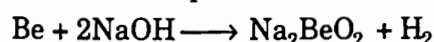
Thus,  $\text{HNO}_3$  can be stored in a vessel made of Al or Be.

- Both form electron-deficient hydrides and volatile chlorides.  $\text{BeH}_2$ ,  $\text{AlH}_3$ , etc, are some electron-deficient hydrides.

- Both form carbides which on hydrolysis give methane.



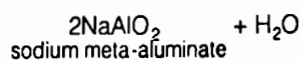
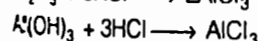
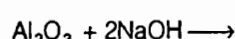
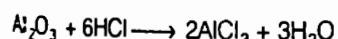
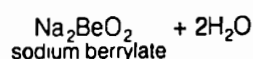
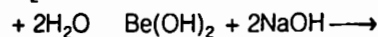
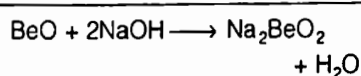
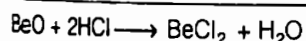
- Both metals dissolve in aqueous alkali evolving  $\text{H}_2$



- Oxides and hydroxides are amphoteric

In dil acid (showing basic nature of oxide or hydroxide)

In alkali solution (showing acidic nature of oxide or hydroxide)



- The two elements have same electronegativity ( $\text{Be} = 1.5$  and  $\text{Al} = 1.5$ ) and their charge/radius ratios (0.064 and 0.060 respectively) are very similar indicating similar field strengths.

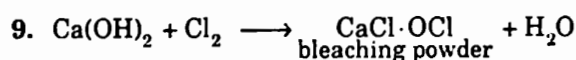
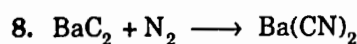
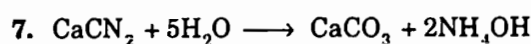
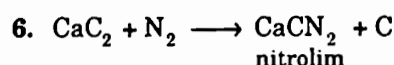
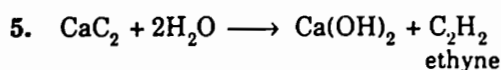
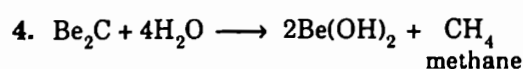
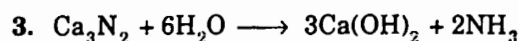
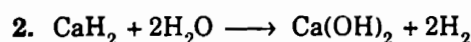
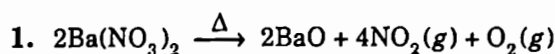
- They have also strong tendency to form complexes:

Be forms tetrahedral complexes as  $\text{BeF}_4^{2-}$  and  $[\text{Be}(\text{C}_2\text{O}_4)_2]^{2-}$

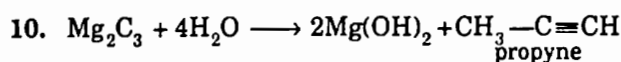
Al forms octahedral complexes like  $\text{AlF}_6^{3-}$  and  $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$ .

## Additional Reactions and Facts of Alkaline Earth Metal Compounds (IIA)

### Reactions



(Bleaching powder contains  $\text{Cl}^-$  and  $\text{ClO}^-$  ions)

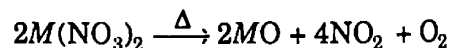


### Important Facts of Alkaline Earth Metals

- Be and Mg are kinetically inert to oxygen and water because of the formation of a surface film of oxide.
- Be and Mg burn in air forming oxides and nitrides ( $\text{BeO}$ ,  $\text{MgO}/\text{Be}_3\text{N}_2$ ,  $\text{Mg}_3\text{N}_2$ ). Ca, Sr and Ba are readily attacked by air forming oxides and nitrides.
- Alkaline earth metals dissolve in liquid  $\text{NH}_3$  to give deep blue black solutions from which ammoniates  $[\text{M}(\text{NH}_3)_6]^{2+}$  can be recovered.
- Metals are electropositive and strong reducing agents. The particularly less negative value for Be arises from the large hydration energy associated with the small size of  $\text{Be}^{2+}$  and the relatively large value of heat of sublimation.
- The solubility, thermal stability and the basic character of hydroxides increase with atomic number from  $\text{Mg}(\text{OH})_2$  to  $\text{Ba}(\text{OH})_2$ .  $\text{Be}(\text{OH})_2 / \text{BeO}$  is amphoteric.
- Except  $\text{BeX}_2$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ), all other halides  $\text{MX}_2$  are ionic.  $\text{BeX}_2$  exists in gas phase only but in condensed phase it exists as polymer. Solubility in water increases with increase in size of cation.

- Carbonates and bicarbonates decompose on heating.  $\text{BeCO}_3$  is least stable and is kept in the atmosphere of  $\text{CO}_2$ .
- Sulphates are stable to heat.  $\text{BeSO}_4$  and  $\text{MgSO}_4$  are soluble in water but solubility decreases from  $\text{CaSO}_4$  to  $\text{BaSO}_4$ . The greater hydration energies of  $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$  ions overcome the lattice energy factor, and hence sulphates are soluble.

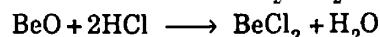
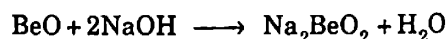
- Oxalates of Ca, Sr, and Ba are sparingly soluble and solubility increases from  $\text{CaC}_2\text{O}_4$  to  $\text{BaC}_2\text{O}_4$ .
- Nitrates decompose to form oxide,  $\text{O}_2$  and  $\text{NO}_2$



- Be shows diagonal relationship to Al.

## Target Practice 2

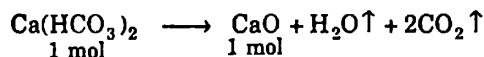
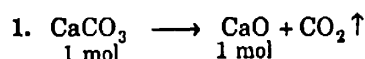
- Mixture containing one mole each of  $\text{CaCO}_3$  and  $\text{Ca}(\text{HCO}_3)_2$  is strongly heated. What is the amount (in moles) of the residue left? .....
- For several thousand years, lime has been used in mortar (a lime, sand and water paste) in building houses, etc. Explain its reaction .....
- (a) What is hybridisation of Be in  $\text{BeF}_2$ ? .....  
(b) When  $\text{BeF}_4^{2-}$  is formed hybridisation of Be changes from ..... to .....
- $\text{BeO}$  is ..... based on following reactions



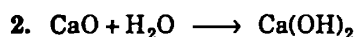
- $\text{CaO}$  is ..... based on following reaction  

$$6\text{CaO} + \text{P}_4\text{O}_{10} \longrightarrow 2\text{Ca}_3(\text{PO}_4)_2$$
- Give the reaction used to prepare  $\text{NaOH}$  from  $\text{Ca}(\text{OH})_2$  in earlier days .....
- $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  is correctly represented as .....
- Name the salt which is used in medicine as a contrast medium for stomach and intestinal X-rays. ....

## Answers



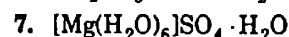
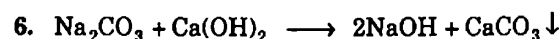
Residue is 2 moles  $\text{CaO}$



- (a)  $sp$  (b)  $sp, sp^3$

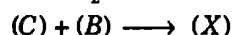
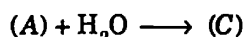
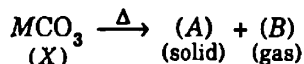
- amphoteric

- basic



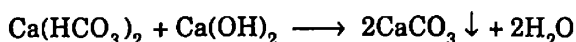
## Practice Exercise 2

- Gas (X) turns lime water milky. Gas (X) also turns acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  green. What is gas (X)?
- Beryllium turns passive in presence of  $\text{HNO}_3$ . Explain.
- Identify (A) to (C) and the metal ion  $\text{M}^{2+}$ .

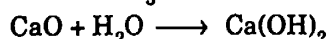


Paste of the salt (X) in conc.  $\text{HCl}$  given green flame on ignition.

- Following reaction is used to remove temporary hardness which is due to dissolved bicarbonates of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$



Actually lime ( $\text{CaO}$ ) is added which in  $\text{H}_2\text{O}$  forms  $\text{Ca}(\text{OH})_2$  and precipitates  $\text{CaCO}_3$



If 10 L of hard water requires 0.56 g of  $\text{CaO}$ , what is temporary hardness in ppm of  $\text{CaCO}_3$  (parts per million—ppm.)?

- $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Ca}(\text{OH})_2$  can't be stored in the same vessel. Explain.

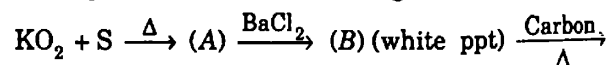
- $\text{Ca}(\text{HCO}_3)_2$  is determined volumetrically by titration with acid. Which of the following indicators is better?

(a) Phenolphthalein

(b) Methyl red

- $\text{Ca}^{2+}$  can be determined by precipitating it as  $\text{CaC}_2\text{O}_4$ , gravimetrically. Calculate percentage of  $\text{Ca}^{2+}$  in a sample, if 0.5 g of  $\text{Ca}^{2+}$  salt gave 1.28 g of  $\text{CaC}_2\text{O}_4$ . ( $\text{Ca} = 40, \text{C} = 12, \text{O} = 16$ )

- Identify (A) to (D) in the following:



(D) gas turns lead acetate paper black.

- Presence of  $\text{CaSO}_4$  causes 'permanent hardness' in water. It can be removed by precipitating it as  $\text{CaCO}_3$  by adding  $\text{Na}_2\text{CO}_3$ . Calculate amount of  $\text{Na}_2\text{CO}_3$  to soften 100 L of hard water which is 200 ppm  $\text{CaCO}_3$ .

10. While moving down the group (in alkaline earth metals) following property decreases  
 (a) radius  
 (b) solubility of hydroxides  
 (c) solubility of sulphates  
 (d) thermal stability of carbonates  
 Choose the correct alternate.

11. (A) is binary oxide of alkaline earth metal. On reaction with HCl, (A) forms solid (B) and liquid (C). (B) gives apple green flame on ignition and liquid (C) decolourises  $\text{KMnO}_4$  in acidic medium. What are (A), (B) and (C)?

12.  $\text{BeCl}_2$  in aqueous solution exists as  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$  rather than  $\text{Be}^{2+}$ . This is acidic in nature. Explain.

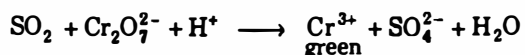
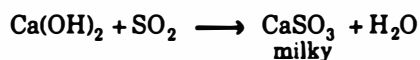
13. Arrange  $\text{BeCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$  and  $\text{BaCl}_2$  in increasing  
 (i) tendency of hydrolysis  
 (ii) lattice energy  
 (iii) solubility in  $\text{H}_2\text{O}$   
 (iv) covalent nature.

14. Match the following chlorides with the colour they impart on ignition in flame:

| Salt               | Colour in flame |
|--------------------|-----------------|
| 1. $\text{CaCl}_2$ | (A) Apple green |
| 2. $\text{SrCl}_2$ | (B) Brick red   |
| 3. $\text{BaCl}_2$ | (C) Crimson red |

### Answers

1. Gas (X) is  $\text{SO}_2$



2.  $\text{HNO}_3$  is an oxidising agent. It oxidises Be to BeO. This, oxide layer prevents attack of  $\text{HNO}_3$  on it. Hence, Be turns passive.

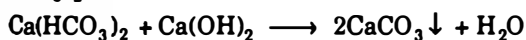
3. (X) :  $\text{BaCO}_3$ ,  $\text{M}^{2+}$  :  $\text{Ba}^{2+}$  (A) : BaO (B) :  $\text{CO}_2$   
 (C) :  $\text{Ba}(\text{OH})_2$

4.  $\text{CaO} \xrightarrow{56 \text{ g}} \text{Ca}(\text{OH})_2 \xrightarrow{0.56 \text{ g}} \underset{200 \text{ g}}{2\text{CaCO}_3}$   
 2.00 g in  $10^4 \text{ mL H}_2\text{O}$

$10^4 \text{ mL H}_2\text{O}$  hardness = 2 g

$10^6 \text{ mL}$  water has hardness = 200 ppm

5.  $\text{Ca}(\text{HCO}_3)_2$  behaves as an acid with  $\text{Ca}(\text{OH})_2$



Hence, neutralisation takes place.

6. Methyl red is only used. Phenolphthalein does not indicate any colour change.

7. 80% pure.

8. (A) :  $\text{K}_2\text{SO}_4$  (B) :  $\text{BaSO}_4$  (C) : BaS (D) :  $\text{H}_2\text{S}$

9.  $\text{Na}_2\text{CO}_3 + \text{CaSO}_4 \longrightarrow \underset{100 \text{ g}}{\text{CaCO}_3 \downarrow} + \underset{100 \text{ g}}{\text{Na}_2\text{SO}_4}$

(1 million) =  $10^6 \text{ mL}$  of hard water has = 200 g  $\text{CaCO}_3$

$100 \text{ L} = 10^5 \text{ mL}$  of hard water has = 20 g  $\text{CaCO}_3$

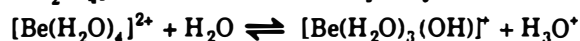
If hardness is 100 g,  $\text{Na}_2\text{CO}_3$  required = 106 g

If hardness is 20 g,  $\text{Na}_2\text{CO}_3$  required = 21.2 g

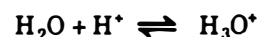
10. (c)

11. (A) :  $\text{BaO}_2 \rightleftharpoons \text{Ba}^{2+} + \text{O}_2^{2-}$  (B) :  $\text{BaCl}_2$  (C) :  $\text{H}_2\text{O}_2$

12.  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$  is acidic because of hydrolysis.



This happens because the Be—O bond is very strong, and this weakens the O—H bond and thus, proton is lost.



13. (i)  $\text{BaCl}_2 < \text{SrCl}_2 < \text{CaCl}_2 < \text{MgCl}_2 < \text{BeCl}_2$   
 (ii)  $\text{BaCl}_2 < \text{SrCl}_2 < \text{CaCl}_2 < \text{MgCl}_2 < \text{BeCl}_2$   
 (iii)  $\text{BeCl}_2 < \text{MgCl}_2 < \text{CaCl}_2 < \text{SrCl}_2 < \text{BaCl}_2$   
 (iv)  $\text{BaCl}_2 < \text{SrCl}_2 < \text{CaCl}_2 < \text{MgCl}_2 < \text{BeCl}_2$

14. 1—(B) 2—(C) 3—(A)

# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** What is biological role of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions?

**Solution**  $\text{Mg}^{2+}$  ions are concentrated in animal cells, and  $\text{Ca}^{2+}$  are concentrated in the body fluids outside the cell.  $\text{Mg}^{2+}$  is important in chlorophyll, in the green parts of plants.

$\text{Ca}^{2+}$  is important in bones and teeth as apatite  $\text{Ca}_3(\text{PO}_4)_2$  and the enamel on teeth as fluoroapatite  $[\text{3}(\text{Ca}_3(\text{PO}_4)_2) \cdot \text{CaF}_2]$ .

$\text{Ca}^{2+}$  ions are important in blood clotting, and are required to trigger the contraction of muscles and to maintain the regular beating of heart.

**Problem 2.** Beryllium gives a compound X with the following percentage composition : Be—6.1%; N—37.8% Cl—48%, H—8.1%. Molecular weight of (X) is  $148 \text{ g mol}^{-1}$  and that of Be is  $9 \text{ g mol}^{-1}$ .

- What is the molecular formula of the compound?
- In aqueous solution, 1 mole of the compound reacts with 2 moles of  $\text{AgNO}_3$  giving white ppt. What is structural formula of (X)?

**Solution**

| Atom | Atomic weight (A) | %    | %/A  | Simplest ratio |
|------|-------------------|------|------|----------------|
| Be   | 9                 | 6.1  | 0.68 | 1              |
| N    | 14                | 37.8 | 2.70 | 4              |
| Cl   | 35.5              | 48.0 | 1.35 | 2              |
| H    | 1                 | 8.1  | 8.10 | 12             |

- Molecular formula is  $\text{BeN}_4\text{Cl}_2\text{H}_{12}$ .
- Since, 1 mole of X reacts with 2 moles of  $\text{AgNO}_3$ , hence two Cl are outside the complex. Since, there are four N and twelve H, this indicates four  $\text{NH}_3$  molecules attached to Be. This gives structural formula as:



**Problem 3.** A student suggested that calcium should be made if calcium oxide is reacted with aluminium powder. Was the student correct?

$$\Delta G_f^\circ (\text{CaO}) = -604.2 \text{ kJ mol}^{-1},$$

$$\Delta G_f^\circ (\text{Al}_2\text{O}_3) = -1582.4 \text{ kJ mol}^{-1}$$

**Solution** A given reaction is spontaneous, if  $\Delta G_f^\circ$  is negative.

$$3\text{CaO} + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 3\text{Ca}$$

$$\Delta G_f^\circ = \Delta G_f^\circ (\text{Al}_2\text{O}_3) - 3\Delta G_f^\circ (\text{CaO})$$

$$= -1582.4 - 3(-604.2)$$

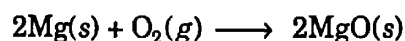
$$= -1582.4 + 1812.6$$

$$= +230.2 \text{ kJ mol}^{-1}$$

The positive sign tells us that the reaction cannot occur under standard conditions.

**Note :** Under non-standard conditions e.g., under high temperatures,  $\Delta G$  is negative and reaction takes place.  $\Delta G_f^\circ (\text{element}) = 0$ .

**Problem 4.** 0.2 g of magnesium ribbon was placed in a crucible and heated with the lid on until the magnesium began to burn rapidly. At the end of the experiment there was 0.3 g of a white powder left. Show that this result does not agree with the equation:



What might have gone wrong?

**Solution**

$$\begin{array}{ccc} 2\text{Mg(s)} & + \text{O}_2(\text{g}) & \longrightarrow 2\text{MgO(s)} \\ 2 \times 24 \text{ g} & & 2 \times 40 \text{ g} \end{array}$$

$$48 \text{ g of Mg gives} = 80 \text{ g of MgO}$$

$$0.2 \text{ g of Mg gives} = \frac{80}{48} \times 0.2$$

$$= 0.33 \text{ g of MgO}$$

But residue left = 0.30 g (given)

Hence, the results are not in accordance with this equation.

It can be due to

- some MgO may have escaped as vapours
- some Mg may not have reacted
- some  $\text{Mg}_3\text{N}_2$  can be formed.

**Problem 5.** Give the trends in solubilities of chlorides, carbonates, sulphates and hydroxides of alkaline earth metals.

**Solution**

|    | Chlorides     | Carbonates    | Sulphates     | Hydroxides    |
|----|---------------|---------------|---------------|---------------|
| Be | least soluble | most soluble  | most soluble  | least soluble |
| Mg | ↓             | ↑             | ↑             | ↓             |
| Ca |               |               |               |               |
| Sr | ↓             | ↑             | ↑             | ↓             |
| Ba | most soluble  | least soluble | least soluble | most soluble  |

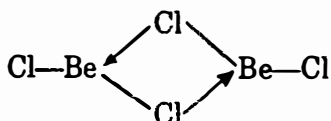
**Problem 6.** What is the importance of calcium and magnesium carbonates and hydrogen carbonates in making water hard or soft?

**Solution** When slightly acidic rain water percolates through carbonate rocks, some of the rocks dissolve.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions are dissolved in the water. It is these ions which give scum with soap or make scale (white deposit) when hard water is boiled.

**Problem 7.** Explain anomalous behaviour of beryllium.

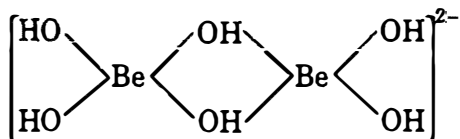
**Solution**

- It is extremely small in size and as determined by Fajan's rule, smaller cations tend to polarise larger anion and thus,  $\text{Be}^{2+}$  forms covalent compounds.
- Be has high electronegativity and compounds like  $\text{BeF}_2$  and  $\text{BeO}$  are covalent.
- $\text{BeX}_2$  exists as polymeric  $(\text{BeX}_2)_n$  in solid state and coordination number = 4 is shown in which each halogen forms



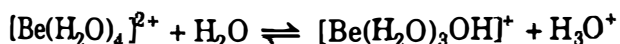
one normal covalent bond, and uses a lone pair to form a coordinate bond.

- In water, beryllium salts are extensively hydrolysed to give a series of hydroxo complexes of the type :



If alkali is added to these solutions, the polymers break down to form  $[\text{Be}(\text{OH})_4]^{2-}$  — a tetrahedral structure.

- $\text{Be}^{2+}$  salts are extensively hydrated due to larger (charge/radius) ratio (called charge density).  $[\text{Be}(\text{H}_2\text{O})_4] \text{SO}_4$ ,  $[\text{Be}(\text{H}_2\text{O})_4](\text{NO}_3)_2$  and  $[\text{Be}(\text{H}_2\text{O})_4] \text{Cl}_2$  are known. These salts are acidic due to following equilibrium :



**Problem 8.** Give a comparison of the elements Be and Al.

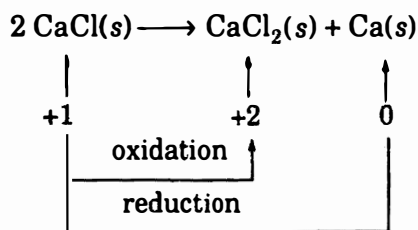
**Solution** Be [2nd period, group 2 (IIA)] and Al [3rd period, group 13 (IIIA)] show diagonal relationship. Be differs in most of the properties of its group but resembles Al (diagonally placed to Be) in following respects:

| Properties          | Explanations                                                                                                                                                                                                                            |
|---------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| With $\text{HNO}_3$ | Both metals are rendered passive and do not dissolve due to formation of oxide layer.                                                                                                                                                   |
| With alkali         | Both dissolve in alkali giving off $\text{H}_2$ .<br>$2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaAlO}_2 + 3\text{H}_2$<br>$\text{Be} + 2\text{NaOH} \longrightarrow \text{Na}_2\text{BeO}_2 + \text{H}_2$ |
| Amphoteric nature   | Both metals react with acid and base and thus are amphoteric.                                                                                                                                                                           |
| Oxides              | Both $\text{BeO}$ and $\text{Al}_2\text{O}_3$ are amphoteric.                                                                                                                                                                           |
| Chlorides           | $\text{BeCl}_2$ and $\text{AlCl}_3$ both are electron deficient and thus are Lewis acids.                                                                                                                                               |

**Problem 9.** The standard enthalpy of formation  $\Delta H_f^\circ$ , of hypothetical  $\text{CaCl}(\text{s})$  theoretically found to be  $-188 \text{ kJ mol}^{-1}$  and that of  $\text{CaCl}_2(\text{s})$   $-795 \text{ kJ mol}^{-1}$ . Calculate the value of standard heat of reaction for the following disproportionation reaction:



**Solution** A disproportionation reaction is that in which the same species (in this case  $\text{Ca}^+$ ) is oxidised as well as reduced.



To determine standard heat of reaction, we use

$$\Delta H^\circ = \Delta H_f^\circ (\text{products}) - \Delta H_f^\circ (\text{reactants})$$

and  $\Delta H_f^\circ$  of the element = 0

$$\begin{aligned}
 \text{Thus, } \Delta H^\circ &= \Delta H_f^\circ (\text{CaCl}_2) + \Delta H_f^\circ (\text{Ca}) - 2\Delta H_f^\circ (\text{CaCl}) \\
 &= (-795 + 0) - (-2 \times 188) \\
 &= -419 \text{ kJ mol}^{-1}
 \end{aligned}$$

This shows that  $\text{CaCl}(\text{s})$  does not exist and any synthetic route to get  $\text{MX}$  in case of the alkaline earth metals will result in the formation of  $\text{MX}_2$ .

# Master Exercises

## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

1. Arrange Be, Ca, Ba, Ra in increasing order of  
(a) size (b) ionisation energy  
(c) electronegativity (d) electron-affinity
2. Arrange alkaline-earth metal chlorides in increasing  
(a) covalent nature (b) melting point  
(c) lattice energy (d) thermal stability
3. Compare thermal stability of  
(a)  $\text{NaHCO}_3$  and  $\text{Ca}(\text{HCO}_3)_2$   
(b)  $\text{CaCO}_3$  and  $\text{Na}_2\text{CO}_3$   
(c)  $\text{BeCO}_3$  and  $\text{Li}_2\text{CO}_3$   
(d)  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$
4. When magnesium burns in air, it forms both an oxide and nitride. Write balanced equations.
5. In the preparation of barium oxide by thermal decomposition of barium carbonate, why is carbon added to the reaction mixture?
6. What is sorel cement?

### Analytical Questions

1. Do you know of a biologically important molecule in which magnesium atoms are held in a position by organic groups?
2. Beryllium chloride exists as  $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$  due to solvation (hydration). What is the hydrated cation? Does it behave as an acid or base, explain?
3.  $\text{Ca}(\text{OH})_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 \downarrow + 2\text{NaOH}$

This reaction made the basis of manufacturing of NaOH in earlier days and pH of the solution was found to be greater than 14. What do you think about the completeness of reaction? Explain.

4. When  $\text{BeCl}_2$  is hydrolysed, there is formation of fumes, explain.
5. (a) Describe how the following properties vary on descending group IA and IIA (alkali and alkaline

earth metals) and state how these properties differ between the two groups?

- (i)  $(IE)_1$  and  $(IE)_2$
  - (ii) cationic radii
  - (iii) rates of reaction with cold water
- (b) For the same s-block elements, discuss :
- (i) action of heat on their nitrates
  - (ii) the crystal structures of their chlorides, XY type only.
6. Compare the chemistries of Mg and Ca with reference to the following :
    - (i) solubilities of their sulphates in water
    - (ii) the thermal stabilities of their carbonates
    - (iii) the reactions of their oxides with  $\text{H}_2\text{O}$ .
  7. (A) is binary electrolyte of a divalent cation. (A) on reaction with  $\text{H}_2\text{SO}_4$  gave a white ppt. (B) and a colourless liquid (C) that can decolourise  $\text{KMnO}_4$  in acidic medium. 1.69 g of (A) gave 2.33 g of (B). What are (A), (B) and (C) and explain reactions?
  8. "The chemistry of beryllium is not essentially ionic." Justify the statement by making reference to the nature of oxide, chloride and fluoride of beryllium.
  9. Comment on each of the following observations
    - (a)  $E^\circ$  for the reaction,  $M^{2+}(\text{aq}) + 2e^- \longrightarrow M(\text{s})$  is nearly constant ( $M = \text{Ca, Sr, Ba}$ ).
    - (b) LiF is least soluble among the fluorides of alkali metals.
  10. How would you explain?
    - (a) BeO is insoluble but  $\text{BeSO}_4$  is soluble in water.
    - (b) BaO is soluble but  $\text{BeSO}_4$  is insoluble in water.
    - (c) LiI is more soluble than KI in ethanol.
    - (d)  $\text{NaHCO}_3$  is isolated in solid state but  $\text{Ca}(\text{HCO}_3)_2$  is not isolated in solid state.
  11. Make distinction between in terms of action of heat
    - (a)  $\text{Na}_2\text{CO}_3$  and  $\text{CaCO}_3$
    - (b)  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
    - (c)  $\text{Ca}(\text{NO}_3)_2$  and  $\text{NaNO}_3$

**NCERT Problems**

- Compare the solubility and thermal stability of the following compounds of the alkali metals with those of the alkaline earth metals.  
(a) nitrates (b) carbonates  
(c) sulphates
- Mention the general trends in group 1 and in group 2 with increasing atomic number with respect to  
(a) density (b) melting point  
(c) atomic size (d) ionisation enthalpy
- How do the following properties change on moving from group I to group 2 in the Periodic Table?  
(i) Atomic size (ii) Ionisation enthalpy  
(iii) Density (iv) Melting point
- Like lithium in group I, beryllium shows anomalous behaviour in group 2. Write three such properties of beryllium which make it anomalous in the group.
- Beryllium exhibits some similarities with aluminium. Point out three such properties.
- The chemistry of beryllium is not essentially ionic. Justify the statement by making a reference to the nature of oxide, chloride and fluoride of beryllium.
- Name the chief forms of occurrence of magnesium in nature. How is magnesium extracted from one of its ores?
- Commercial aluminium always contains some magnesium. Name two such alloys of aluminium. What properties are imparted by the addition of magnesium to these alloys?
- The enthalpy of formation of hypothetical  $\text{CaCl(s)}$  theoretically found to be  $-118 \text{ kJ mol}^{-1}$  and the  $\Delta_f H^\ominus$  for  $\text{CaCl}_2\text{(s)}$  is  $-795 \text{ kJ mol}^{-1}$ . Calculate the  $\Delta_f H^\ominus$  for the disproportionation reaction.  
$$2\text{CaCl(s)} \longrightarrow \text{CaCl}_2\text{(s)} + \text{Ca(s)}$$

[Hint.  $\Delta_f H^\ominus(\text{CaCl}_2) - 2\Delta_f H^\ominus(\text{CaCl})$   
 $= -795 + 2 \times 188$   
 $= -419 \text{ kJ mol}^{-1}$ ]
- Compare and contrast the chemistry of group 1 metals with that of group 2 metals with respect to  
(i) nature of oxides  
(ii) solubility and thermal stability of carbonates  
(iii) polarizing power of cations  
(iv) reactivity and reducing power
- Describe the importance of the following  
(i) limestone (ii) cement  
(iii) Plaster of Paris
- Mention the main constituents of Portland cement.
- What happens when  
(i) magnesium is burnt in air?  
(ii) quicklime is heated with silica?  
(iii) chlorine reacts with slaked lime?  
(iv) calcium nitrate is heated?
- Draw the structure of  
(i)  $\text{BeCl}_2$  (vapour) (ii)  $\text{BeCl}_2\text{(s)}$
- List the raw materials required in the manufacture of Portland cement. What is the role of gypsum in it?
- Differentiate between (a) quick-lime (b) lime-water (c) slaked-lime.
- How is plaster of Paris prepared? Describe its chief property due to which it is widely used.
- How would you explain?  
(i)  $\text{BeO}$  is insoluble but  $\text{BeSO}_4$  is soluble in water  
(ii)  $\text{BaO}$  is soluble but  $\text{BaSO}_4$  is insoluble in water  
(iii)  $\text{LiI}$  is more soluble than  $\text{KI}$  in ethanol  
(iv)  $\text{NaHCO}_3$  is known in solid state but  $\text{Ca(HCO}_3)_2$  is not isolated in solid state
- Contrast the action of heat on the following and explain your answer  
(i)  $\text{Na}_2\text{CO}_3$  and  $\text{CaCO}_3$   
(ii)  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$   
(iii)  $\text{Ca(NO}_3)_2$  and  $\text{NaNO}_3$
- Complete the following equations for the reaction between  
(i)  $\text{Ca} + \text{H}_2\text{O}$  (ii)  $\text{Ca(OH)}_2 + \text{Cl}_2$   
(iii)  $\text{BeO} + \text{NaOH}$  (iv)  $\text{BaO}_2 + \text{H}_2\text{SO}_4$

**Exercise 2****(Stage 2 : High Skill Problem Solving)****Only One Option Correct**

- Mg and Zn does not resemble in following properties  
(a) oxides are amphoteric  
(b) carbonates on heating form metal oxides  
(c) widely used as electrodes  
(d) used to prevent corrosion
- When  $\text{Cl}_2$  is passed into moist slaked lime, compound formed is  
(a)  $\text{CaO}_2\text{Cl}_2$  (b)  $\text{CaO}_2\text{Cl}$   
(c)  $\text{CaOCl}_2$  (d)  $\text{CaCl}_2\text{O}_4$
- A colourless solid (X) on heating evolved  $\text{CO}_2$  and also gave a white residue, soluble in water. Residue also gave  $\text{CO}_2$  when treated with dilute acid. (X) is



- (a)  $\text{Na}_2\text{CO}_3$  (b)  $\text{CaCO}_3$   
(c)  $\text{Ca}(\text{HCO}_3)_2$  (d)  $\text{NaHCO}_3$
4. II A (alkaline earth metals) and II B (zinc family) resemble  
(a)  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  is isomorphous with  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$   
(b) II A and II B cations are not precipitated by  $\text{H}_2\text{S}$  in acidic medium  
(c) both (a) and (b)  
(d) None of the above
5. Be and Al show diagonal relationship hence, both have  
(a) same degree of electronegativity  
(b) amphoteric nature of oxides  
(c) approximately same charge/radius ratio  
(d) all the properties above
6. Be and Al do not resemble in  
(a) both become passive on reaction with  $\text{HNO}_3$  due to formation of oxide layer  
(b) their chlorides are Lewis bases  
(c) chlorides exist in polymeric form  
(d) hydroxides are soluble in alkali as well as in acid
7. Going down to II A group, following properties increase except  
(a) solubility of hydroxides in  $\text{H}_2\text{O}$   
(b) hydration energy  
(c) thermal stability of carbonates  
(d) ionic radius
8. Identify the correct statement.  
(a) Gypsum is obtained by heating plaster of Paris.  
(b) Plaster of Paris can be obtained by hydration of gypsum.  
(c) Plaster of Paris contains higher percentage of calcium than does gypsum.  
(d) Plaster of Paris is obtained from gypsum by oxidation.
9. Following are the ionisation potential values of  
( $I_1$ )  $899 \text{ kJ mol}^{-1}$ , ( $I_2$ )  $1757 \text{ kJ mol}^{-1}$ ,  
( $I_3$ )  $15000 \text{ kJ mol}^{-1}$   
(a) Na (b) K  
(c) Be (d) Ne
10. Which is most stable out of the following?  
(a)  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$  (b)  $[\text{Mg}(\text{H}_2\text{O})_4]^{2+}$   
(c)  $[\text{Ca}(\text{H}_2\text{O})_4]^{2+}$  (d)  $[\text{Sr}(\text{H}_2\text{O})_4]^{2+}$
11. Lattice energy of II A group compounds (oxides, carbonates, fluorides)  
(a) decreases as size of the ion increases  
(b) increases as size of the ion increases  
(c) constant for a given type of anion  
(d) all the above are incorrect
12. Which of the following statements are true about II A group elements?  
(a) All form nitrides in air  
(b) Be is amphoteric  
(c)  $\text{MH}_2$  is ionic 'salt-like' hydride  
(d) All the above are correct statements
13. Choose the incorrect statement.  
(a)  $\text{BeCO}_3$  is kept in the atmosphere of  $\text{CO}_2$  since it is least thermally stable  
(b) Be dissolves in alkali forming  $[\text{Be}(\text{OH})_4]^{2-}$   
(c)  $\text{BeF}_2$  forms complex ion with NaF in which Be goes with cation  
(d)  $\text{BeF}_2$  forms complex ion with NaF in which Be goes with anion
14. Which are true statements about s-block elements?  
(a) Metals are obtained by the electrolysis of fused chlorides  
(b) Only one type of valency, +1 for I A and +2 for II A, is shown  
(c) Oxides are basic except  $\text{BeO}$   
(d) All the above are correct statements
15. Which cannot be used to generate  $\text{H}_2$ ?  
(a)  $\text{Al} + \text{NaOH}$  (b)  $\text{Zn} + \text{NaOH}$   
(c)  $\text{Mg} + \text{NaOH}$  (d)  $\text{LiH} + \text{H}_2\text{O}$
16. Portland cement does not contain  
(a)  $\text{CaSiO}_4$  (b)  $\text{CaSiO}_3$   
(c)  $\text{Ca}_3\text{Al}_2\text{O}_6$  (d)  $\text{Ca}_3(\text{PO}_4)_2$
17. Setting of plaster of Paris is  
(a) oxidation with atmospheric oxygen  
(b) combination with atmospheric  $\text{CO}_2$   
(c) dehydration  
(d) hydration to yield another hydrate
18. Mixture of  $\text{MgCl}_2$  and  $\text{MgO}$  is called  
(a) Portland cement (b) Sorel's cement  
(c) double salt (d) None of these
19. Setting of cement is  
(a) exothermic reaction  
(b) endothermic reaction  
(c) neither endothermic nor exothermic  
(d) None of the above
20. Which is main constituent of egg-shell?  
(a)  $\text{CaCO}_3$  (b)  $\text{CaSiO}_3$   
(c)  $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$  (d)  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
21. The deliquescent among the following is  
(a)  $\text{CaCl}_2$  (b)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$   
(c)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (d)  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$
22. Which is incorrect statement?  
(a) The heats of hydration of the divalent alkaline earth metal ions decrease with an increase in their ionic size.  
(b)  $\text{NaNO}_3$  forms  $\text{Na}_2\text{O}$  on heating  
(c) Hydration of alkali metal ion is less than that of II A.

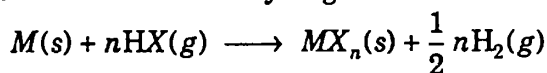
- (d) Alkaline earth metal ions, because of their much larger charge to size ratio, exert a much stronger electrostatic attraction on the oxygen of water molecule surrounding them.
23. Which is used for fixing atmospheric nitrogen?  
 (a)  $\text{CaCN}_2$  (nitrolim) (b)  $\text{Li}_3\text{N}$   
 (c)  $\text{Mg}_3\text{N}_2$  (d) All of these
24.  $\text{BaC}_2 + \text{N}_2 \xrightarrow{\Delta} (A)$   
 $\text{CaC}_2 + \text{N}_2 \xrightarrow{\Delta} (B)$   
 (A) and (B) are  
 (a)  $\text{BaCN}_2$ ,  $\text{CaCN}_2$  (b)  $\text{Ba}(\text{CN})_2$ ,  $\text{Ca}(\text{CN})_2$   
 (c)  $\text{Ba}(\text{CN})_2$ ,  $\text{CaCN}_2$  (d) None is correct
25. Estimation of calcium and magnesium is done by  
 (a) EDTA (b) oxalate  
 (c) phosphate (d) None of these
26. Which of the following is/are correct statement(s)?  
 (a)  $\text{Ca}_3(\text{PO}_4)_2$  in part of bones  
 (b)  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$  is part of enamel on teeth  
 (c)  $\text{Ca}^{2+}$  ions are important in blood clotting  
 (d) All of the above are correct
27. 1 mole of a substance (X) was treated with an excess of water. 2 moles of readily combustible gas were produced along with solution which when reacted with  $\text{CO}_2$  gas produced a white turbidity. The substance (X) could be  
 (a) Ca (b)  $\text{CaH}_2$   
 (c)  $\text{Ca}(\text{OH})_2$  (d)  $\text{Ca}(\text{NO}_3)_2$
28. A basic refractory material among the following is  
 (a)  $\text{Al}_2\text{O}_3$  (b)  $\text{SiO}_2$   
 (c)  $\text{Fe}_2\text{O}_3$  (d)  $\text{CaO}$
29. In water  
 (a) temporary hardness is due to the bicarbonates of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$   
 (b) permanent hardness is due to chlorides and sulphates of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$   
 (c) hardness can be removed by adding phosphates  
 (d) all of the above properties are true
30.  $\text{Na}_2[\text{Be}(\text{OH})_4]$  is formed when  
 (a) BeO reacts with NaOH solution  
 (b) Be reacts with NaOH solution  
 (c) both (a) and (b) correct  
 (d) None of the above is correct
31. Which is used to treat acid indigestion?  
 (a)  $\text{Be}(\text{OH})_2$  (b) KOH  
 (c)  $\text{Mg}(\text{OH})_2$  (d)  $\text{Ca}(\text{OH})_2$
32. Which is not obtained when metal carbides react with  $\text{H}_2\text{O}$ ?  
 (a)  $\text{Al}_4\text{C}_3 + \text{H}_2\text{O} \longrightarrow \text{CH}\equiv\text{CH}$   
 (b)  $\text{CaC}_2 + \text{H}_2\text{O} \longrightarrow \text{CH}\equiv\text{CH}$   
 (c)  $\text{Mg}_2\text{C}_3 + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{C}\equiv\text{CH}$   
 (d)  $\text{Be}_2\text{C} + \text{H}_2\text{O} \longrightarrow \text{CH}_4$
33. Select correct statement(s).  
 (a) Beryllium and magnesium hydride are covalent and polymeric  
 (b)  $\text{CaH}_2$ ,  $\text{SrH}_2$  and  $\text{BaH}_2$  are ionic  
 (c)  $\text{BeH}_2$  contains three-centre two-electron bond  
 (d) All the above are correct statements
34. Select correct statement(s).  
 (a)  $\text{CaCO}_3$  is more soluble in a solution of  $\text{CO}_2$  than in  $\text{H}_2\text{O}$   
 (b)  $\text{NaCO}_3$  is converted to  $\text{Na}_2\text{O}$  and  $\text{CO}_2$  on heating  
 (c)  $\text{Li}_2\text{CO}_3$  is thermally stable  
 (d) Presence of  $\text{CaCl}_2$  or  $\text{CaSO}_4$  in water causes temporary hardness
35. Select correct statement(s).  
 (a)  $\text{Mg}^{2+}$  ions are necessary for the activation of phosphate transfer enzymes.  
 (b) Mg is present in chlorophyll used in photosynthesis in green plants.  
 (c) Operation of  $\text{Na}^+ - \text{K}^+$  pumps is biological.  
 (d) All the above are correct statements
36. A metal *M* readily forms water soluble  $\text{MSO}_4$ . It also forms oxide  $\text{MO}$  which becomes inert on heating. Hydroxide  $\text{M}(\text{OH})_2$  is insoluble in water but soluble in NaOH solution. What is *M*?  
 (a) Mg (b) Ba  
 (c) Ca (d) Be
37. Which one of the following has magnesium?  
 (a) Vitamin  $\text{B}_{12}$  (b) Chlorophyll  
 (c) Haemocyanin (d) Carbonic anhydrase
38. In which of the following the hydration energy is higher than the lattice energy?  
 (a)  $\text{BaSO}_4$  (b)  $\text{MgSO}_4$   
 (c)  $\text{RaSO}_4$  (d)  $\text{SrSO}_4$
39. Epsom salt is  
 (a)  $\text{BaSO}_4 \cdot 2\text{H}_2\text{O}$  (b)  $\text{CaSO}_4 \cdot \text{H}_2\text{O}$   
 (c)  $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$  (d)  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
40. Slaked lime and chlorine reacts to produce  
 (a) quick lime  
 (b)  $\text{CaCl}_2$   
 (c)  $\text{CaOCl}_2$   
 (d) mixture of  $\text{CaCl}_2$  and  $\text{Ca}(\text{OCl}_2)$
41. Mg and Li and similar in their properties due to  
 (a) same *e/m* ratio (b) same electron affinity  
 (c) same group (d) same radius
42. Which one of the following hydroxide is insoluble in water?  
 (a)  $\text{Ca}(\text{OH})_2$  (b)  $\text{Ba}(\text{OH})_2$   
 (c)  $\text{Be}(\text{OH})_2$  (d)  $\text{Mg}(\text{OH})_2$
43. The pair of amphoteric hydroxide is  
 (a)  $\text{Al}(\text{OH})_3$ , LiOH (b)  $\text{Be}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$   
 (c)  $\text{B}(\text{OH})_3$ ,  $\text{Be}(\text{OH})_2$  (d)  $\text{Be}(\text{OH})_2$ ,  $\text{Zn}(\text{OH})_2$

44. The pair whose both species are used in antacid medicinal preparation is  
 (a)  $\text{NaHCO}_3$  and  $\text{Mg(OH)}_2$   
 (b)  $\text{Na}_2\text{CO}_3$  and  $\text{Ca(HCO}_3)_2$   
 (c)  $\text{Ca(HCO}_3)_2$  and  $\text{Mg(OH)}_2$   
 (d)  $\text{Ca(OH)}_2$  and  $\text{NaHCO}_3$
45. Lithophone is mixture of  
 (a)  $\text{ZnCO}_3$ ,  $\text{BaCO}_3$  (b)  $\text{ZnS}$ ,  $\text{Na}_2\text{SO}_4$   
 (c)  $\text{ZnSO}_4$ ,  $\text{BaSO}_4$  (d)  $\text{ZnS}$ ,  $\text{BaSO}_4$
46. Gypsum is  
 (a)  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (b)  $\text{CaCO}_3 \cdot 2\text{H}_2\text{O}$   
 (c)  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  (d)  $\text{SiO}_2$
47. Alkaline earth metals are  
 (a) reducing agent (b) dehydrating agent  
 (c) amphoteric (d) oxidising agent
48. A covalent chloride is  
 (a)  $\text{BeCl}_2$  (b)  $\text{NaCl}$   
 (c)  $\text{MgCl}_2$  (d)  $\text{CaCl}_2$
49. Plaster of Paris is hardened by  
 (a) giving out water  
 (b) uniting with water  
 (c) changing into  $\text{CaCO}_3$   
 (d) liberating  $\text{CO}_2$
50. Which of the following halide of calcium is insoluble in water?  
 (a)  $\text{CaCl}_2$  (b)  $\text{CaI}_2$   
 (c)  $\text{CaF}_2$  (d)  $\text{CaBr}_2$
51. The substance used as pigment in paint is  
 (a) borax (b) alumina  
 (c) lithophone (d) None of these
52. Lightest alkaline earth metal is  
 (a) Be (b) Mg  
 (c) Ca (d) Sr
53. Which of the following is not an ore of magnesium?  
 (a) Carnallite (b) Magnesite  
 (c) Dolomite (d) Gypsum
54. The activity of alkaline earth metals as reducing agent  
 (a) decreases from Be to Ba  
 (b) increases from Be to Ba  
 (c) increase from Be to Ca and decreases from Ca to Ba  
 (d) decreases from Be to Ca and increases from Ca to Ba
55. Magnalium contains  
 (a) aluminium + magnesium  
 (b) magnesium + copper  
 (c) magnesium + iron  
 (d) magnesium + silver
56. Be in  $\text{BeCl}_2$  undergoes  
 (a) linear hybridisation  
 (b) trigonal hybridisation  
 (c) tetrahedral hybridisation  
 (d) no hybridisation
57.  $\text{CaCl}_2$  is used as  
 (a) disinfectant (b) desiccant agent  
 (c) medicine (d) None of these
58. The product obtained on fusion of  $\text{BaSO}_4$  and  $\text{Na}_2\text{CO}_3$  is  
 (a)  $\text{BaCO}_3$  (b) BaO  
 (c)  $\text{Ba(OH)}_2$  (d)  $\text{BaHSO}_4$
59. Which of the following is known as dead burnt?  
 (a) Gypsum (b) Plaster of Paris  
 (c) Anhydrite (d) None of these
60. The decomposition temperature is maximum for  
 (a)  $\text{MgCO}_3$  (b)  $\text{CaCO}_3$   
 (c)  $\text{BaCO}_3$  (d)  $\text{SrCO}_3$
61. Bleaching powder loses its power on keeping for a long time because  
 (a) it changes into calcium hypochlorate  
 (b) it changes into calcium chloride and calcium hydroxide  
 (c) it absorbs moisture  
 (d) it changes into calcium chloride and calcium chlorate
62. Among  $\text{Na}^+$ , Na, Mg and  $\text{Mg}^{2+}$  the largest particle is  
 (a)  $\text{Mg}^{2+}$  (b) Mg  
 (c) Na (d)  $\text{Na}^+$
63. The electron affinity of Be is similar to  
 (a) He (b) B  
 (c) Li (d) Na
64. Bleaching action of  $\text{CaOCl}_2$  is due to  
 (a) nascent oxygen (b) chlorine  
 (c)  $\text{HClO}$  (d)  $\text{HCl}$
65. In alkaline earth metal sulphates, the value of hydration energy decreases down the group because of the  
 (a) decrease in size  
 (b) increase in size  
 (c) greater lattice energy  
 (d) None of the above
66. The correct order of increasing ionic character is  
 (a)  $\text{BeCl}_2 < \text{CaCl}_2 < \text{MgCl}_2 < \text{BaCl}_2$   
 (b)  $\text{BeCl}_2 < \text{MgCl}_2 < \text{BaCl}_2 < \text{CaCl}_2$   
 (c)  $\text{BeCl}_2 < \text{BaCl}_2 < \text{MgCl}_2 < \text{CaCl}_2$   
 (d)  $\text{BaCl}_2 < \text{CaCl}_2 < \text{MgCl}_2 < \text{BeCl}_2$
67. Ripening of fruits can be carried out in presence of  
 (a)  $\text{Na}_2\text{SO}_4$  (b) NaCl  
 (c)  $\text{CaCl}_2$  (d)  $\text{CaC}_2$

68. The right order of the solubility of sulphates of alkaline earth metals in water  
 (a)  $\text{Be} > \text{Ca} > \text{Mg} > \text{Ba} > \text{Sr}$   
 (b)  $\text{Mg} > \text{Be} > \text{Ba} > \text{Ca} > \text{Sr}$   
 (c)  $\text{Be} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$   
 (d)  $\text{Mg} > \text{Ca} > \text{Ba} > \text{Be} > \text{Sr}$
69. Burning of Mg is extinguished by  
 (a) throwing  $\text{N}_2$  liquid (b) throwing sand  
 (c) throwing ice (d) throwing water
70. Flame test is not given by  
 (a) Ca (b) Ba  
 (c) Mg (d) Li
71. Lithium shows similarities with magnesium in its chemical behaviour because  
 (a) similar size, greater electronegativity and lower polarising power  
 (b) similar size, same electronegativity and lower polarising power  
 (c) similar size, same electronegativity and similar high polarising power  
 (d) None of the above
72. The element whose electronic configuration is  $1s^2 2s^2 2p^6 3s^2$  is  
 (a) non-metal (b) noble gas  
 (c) metalloid (d) metal
73. On strong heating  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  the product obtained is  
 (a)  $\text{MgCl}_2$  (b)  $\text{MgO}$   
 (c)  $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$  (d)  $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$
74. Which of the following carbonate decompose most easily on heating?  
 (a)  $\text{Rb}_2\text{CO}_3$  (b)  $\text{K}_2\text{CO}_3$   
 (c)  $\text{Na}_2\text{CO}_3$  (d)  $\text{MgCO}_3$
75. The solubilities of carbonates decrease down the magnesium group due to a decrease in  
 (a) lattice energies of solids  
 (b) hydration energies of cations  
 (c) interionic attractions  
 (d) entropy of solution formation
76. The charge/size ratio of a cation determines its polarising power. Which one of the following sequences represents the increasing order of the polarising power of cationic species;  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Be}^{2+}$ ?  
 (a)  $\text{Mg}^{2+} < \text{Be}^{2+} < \text{K}^+ < \text{Ca}^{2+}$   
 (b)  $\text{Be}^{2+} < \text{K}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$   
 (c)  $\text{K}^+ < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Be}^{2+}$   
 (d)  $\text{Ca}^{2+} < \text{Mg}^{2+} < \text{Be}^{2+} < \text{K}^+$
77. What is impurity (as a salt) associated with table salt obtained from sea-water?  
 (a)  $\text{NaHCO}_3$  (b)  $\text{MgCO}_3$   
 (c)  $\text{MgCl}_2$  (d)  $\text{NaI}$
78. Select correct statement(s).  
 (a) Presence of  $\text{MgCl}_2$  in table salt causes it to clump  
 (b) Addition of  $\text{NaHCO}_3$  to table salt converts  $\text{MgCl}_2$  to non-hygroscopic salt  
 (c) Both (a) and (b)  
 (d) None of the above
79. In polymeric  $(\text{BeCl}_2)_n$ , there are  
 (a) three centre two-electron bonds  
 (b) three centre three-electron bonds  
 (c) two centre three-electrons bonds  
 (d) two centre two-electron bonds
80. Be and Al resemble in the following but not in  
 (a) both form electron deficient hydrides  
 (b) both are rendered passive by  $\text{HNO}_3$   
 (c) both form amphoteric oxides  
 (d) both have  $sp$ -hybridisation in their compounds
81. Select incorrect statement.  
 (a)  $\text{NaOH}$  can be stored in a vessel made of Al  
 (b)  $\text{HNO}_3$  can be stored in a vessel made of Be/Al alloy  
 (c)  $\text{HF}$  can be stored in a vessel made of wax  
 (d)  $\text{HF}$  attacks glass
82. Metal carbides on reaction with  $\text{H}_2\text{O}$  from  $\text{CH}_4$ . Carbide can be  
 (a)  $\text{CaC}_2$  (b)  $\text{Mg}_3\text{C}_2$   
 (c)  $\text{Be}_2\text{C}$  (d)  $\text{SiC}$
83. Select correct statement.  
 (a) Be and Al show diagonal relationship  
 (b) Be form tetrahedral complexes  $[\text{Be}(\text{C}_2\text{O}_4)_2]^{2-}$   
 (c) Al forms  $\text{AlF}_6^{3-}$ , an octahedral complex  
 (d) All the above are correct statements

## Brain Twisters

1. Metals reacts with hydrogen halides (such as  $\text{HCl}$ ) to give metal halide and hydrogen :



$$\Delta G^\circ = \Delta G^\circ(\text{MX}_n) - n\Delta G^\circ(\text{HX}(g))$$

$$\Delta G^\circ(\text{HCl}(g)) = -95.1 \text{ kJ mol}^{-1}.$$

What is relative value of  $\Delta G^\circ$  for  $\text{MX}_n$  for the reaction to be product-favoured?

2. A mineral  $\text{Mg}_x\text{Ba}_y(\text{CO}_3)_z$  was analysed as given below:

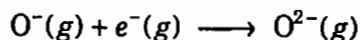
A sample of the mineral was dissolved in excess  $\text{HCl}$  and the solution made up to 100 mL with water. During the process 48 mL of  $\text{CO}_2$  measured at  $25^\circ\text{C}$  and 1 atmosphere pressure were evolved.

A 25.0 mL portion of the resulting solution required 25.0 mL of EDTA solution of 0.02 M to reach end point. A further 25.0 mL portion gave a precipitate of  $\text{BaSO}_4$  of mass 0.058 g on treatment with excess of

dil.  $\text{H}_2\text{SO}_4$ . You may assume that group 2 (alkaline earth metals) metal ions form 1:1 complexes with EDTA.

(Given molar volume of any gas at  $25^\circ\text{C}$  and 1 atmosphere pressure = 24 L)

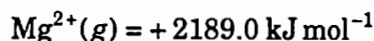
3. Use the following data to calculate second electron affinity of oxygen, i.e., for the process



Is the  $\text{O}^{2-}$  ion stable in the gas phase? Why is it stable in solid  $\text{MgO}$ ?

Heat of sublimation of  $\text{Mg}(s) = +147.7 \text{ kJ mol}^{-1}$

Ionisation energy of  $\text{Mg}(g)$  to form



Bond dissociation energy for  $\text{O}_2 = +498.4 \text{ kJ mol}^{-1}$

First electron affinity of  $\text{O}(g) = -141.0 \text{ kJ mol}^{-1}$

Heat formation of  $\text{MgO}(s) = -601.7 \text{ kJ mol}^{-1}$

Lattice energy of  $\text{MgO} = -3791.0 \text{ kJ mol}^{-1}$

4. A 1.005 g sample of an unknown alkaline earth metal was allowed to react with a volume of chlorine gas that contains  $1.91 \times 10^{22}$   $\text{Cl}_2$  molecules. The resulting metal chloride was analysed for chlorine by dissolving 0.436 g sample in water and adding an excess of  $\text{AgNO}_3(aq)$ . The analysis yielding 1.9126 g of  $\text{AgCl}$ .
- What is the identity of the alkaline earth metal?
  - What is the % of Cl in the alkaline earth chloride.

## Passage Comprehension Questions

### Passage 1

Based on the following analytical data, answer the questions.

A mineral, which can be represented by the formula  $\text{Mg}_x\text{Ba}_y(\text{CO}_3)_z$ , was analysed as described below:

A sample of the mineral was dissolved in excess hydrochloric acid and the solution made up to  $100 \text{ cm}^3$  with water. During the process  $48 \text{ cm}^3$  of carbon dioxide, measured at  $25^\circ\text{C}$  and 1 atmosphere pressure, were evolved.

A  $25.0 \text{ cm}^3$  portion of the resulting solution required  $25.0 \text{ cm}^3$  of EDTA solution of concentration  $0.02 \text{ mole dm}^{-3}$  to reach an end-point. A further  $25.0 \text{ cm}^3$  portion gave a precipitate of barium sulphate of mass 0.058 g on treatment with excess dilute sulphuric acid. You may assume that group-2 metal ions form 1:1 complexes with EDTA.

Molar volume of any gas at  $25^\circ\text{C}$  and 1 atmosphere pressure =  $24 \text{ dm}^3$ .

1. Formula of the mineral is

- $\text{MgBa}(\text{CO}_3)_4$
- $\text{MgBa}(\text{CO}_3)_2$
- $\text{MgBa}(\text{CO}_3)_3$
- $\text{Mg}_2\text{Ba}(\text{CO}_3)_4$

- In the mineral barium ion can be identified by
  - green colour in flame
  - yellow precipitate with  $\text{CrO}_4^{2-}$  solution
  - white precipitate with  $\text{SO}_4^{2-}$
  - all of the above

- Identical mineral of calcium and magnesium ions is
  - dolomite
  - magnesite
  - epsomite
  - talc

### Passage 2

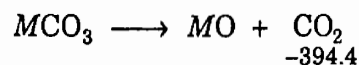
Questions given below are based on the following enthalpy values

The standard enthalpy of formation  $\Delta H_f^\circ$ , of hypothetical  $\text{CaCl}(s)$  theoretically found to be  $-188 \text{ kJ mol}^{-1}$  and that of  $\text{CaCl}_2(s)$   $-795 \text{ kJ mol}^{-1}$ .

- Which of the following compounds is more stable?
  - $\text{CaCl}(s)$
  - $\text{CaCl}_2(s)$
  - Both (a) & (b) are equally stable
  - Nothing can be said
- Select most spontaneous reaction
  - $2\text{CaCl}(s) \longrightarrow \text{CaCl}_2(s) + \text{Ca}(s)$
  - $\text{CaCl}_2(s) + \text{Ca}(s) \longrightarrow 2\text{CaCl}(s)$
  - $\text{CaCl}(s) \longrightarrow \text{Ca}(s) + \text{Cl}(g)$
  - $\text{CaCl}_2(s) \longrightarrow \text{Ca}(s) + \text{Cl}_2(g)$

### Passage 3

$\Delta G^\circ$  values ( $\text{kJ mol}^{-1}$ ) for the following cases can given



|    |         |        |       |
|----|---------|--------|-------|
| Mg | -1028.2 | -568.9 | 64.9  |
| Ca | -1129.2 | 603.4  | 165.9 |
| Ba | -1134.4 | -520.4 | 219.6 |

Answer the following questions

- Maximum value of  $\Delta G^\circ$  is for the reaction when M is
  - Mg
  - Ca
  - Ba
  - equal for all cases
- Thermal stability of the carbonates is in order
  - $\text{MgCO}_3 < \text{CaCO}_3 < \text{BaCO}_3$
  - $\text{BaCO}_3 < \text{CaCO}_3 < \text{MgCO}_3$
  - $\text{MgCO}_3 < \text{BaCO}_3 < \text{CaCO}_3$
  - $\text{CaCO}_3 < \text{BaCO}_3 < \text{MgCO}_3$
- Which is decomposed most easily?
  - $\text{CaCO}_3$
  - $\text{MgCO}_3$
  - $\text{BaCO}_3$
  - Equally
- $\text{BeCO}_3$  decomposes at low temperature. To avoid its decomposition, it is placed in the atmosphere of
  - $\text{N}_2$
  - He
  - Ne
  - $\text{CO}_2$

### Passage 4

Calcium oxide, CaO, is used to remove SO<sub>2</sub> from power plant exhaust."

Based on the above statement, answer the following questions

- In what form CaO removes SO<sub>2</sub> ?  
 (a) CaSO<sub>3</sub> (b) CaSO<sub>4</sub>  
 (c) Ca(HSO<sub>3</sub>)<sub>2</sub> (d) Ca(HSO<sub>4</sub>)<sub>2</sub>
- What mass of SO<sub>2</sub> can be removed using  $1.4 \times 10^3$  kg CaO?  
 (a)  $1.4 \times 10^3$  kg (b)  $1.6 \times 10^3$  kg  
 (c)  $2.2 \times 10^3$  kg (d)  $2.4 \times 10^3$  kg
- Presence of SO<sub>2</sub> from power plant exhaust can be detected by  
 (a) Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> which changes to green  
 (b) MnO<sub>4</sub><sup>-</sup> which changes to colourless  
 (c) both (a) & (b) above  
 (d) None of the above

### Assertion & Reason

Codes :

- Both **A** and **R** are true and **R** is the correct explanation of **A**.
  - Both **A** and **R** are true but **R** is not the correct explanation of **A**.
  - A** is true but **R** is false.
  - A** is false but **R** is true.
- Assertion (A) :** BaSO<sub>4</sub> is likely insoluble in water but readily dissolves in solution of sodium salt of ethylene diamine tetra acetic acid (EDTA).  
**Reason (R) :** Ba<sup>2+</sup> forms a very stable complex with the anion of the sodium salt EDTA which is water soluble.
  - Assertion (A) :** Temporary hardness can be removed by addition of lime.  
**Reason (R) :** Ca(HCO<sub>3</sub>)<sub>2</sub> in hard water is converted to insoluble CaCO<sub>3</sub> on moderate heating.
  - Assertion (A) :** Group 2 metals have higher melting points when compared to the group 1 metals.  
**Reason (R) :** +2 charge on the cations in the metallic lattice causes them to be more strongly attracted to the 'sea of electrons' and making it difficult to pull them apart.
  - Assertion (A) :** The metals of group 2 (except Be) form ionic compounds.  
**Reason (R) :** Electropositive character and the reducing property increase on moving down the group.
  - Assertion (A) :** Divalent compounds of alkaline earth metals are diamagnetic.  
**Reason (R) :** M<sup>2+</sup> ions of group 2 have noble gas configuration.

### True & False

- When CO<sub>2</sub> is passed into lime water, white turbidity appears which dissolves in excess of CO<sub>2</sub>.
- SO<sub>2</sub> turns lime water milky.
- [Be(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> is an acid.
- Solubility of sulphates of alkaline earth metals increases going down the group.
- Mg<sub>2</sub>C<sub>3</sub> on reaction with water forms propane.
- CaCO<sub>3</sub> is the main constituent of egg shell.
- EDTA is used to estimate Ca and Mg.
- Permanent hardness is due to dissolved bicarbonates of Ca<sup>2+</sup> and Mg<sup>2+</sup>.
- BeCl<sub>2</sub> is a nucleophile.
- BeO and Al<sub>2</sub>O<sub>3</sub> are amphoteric.
- Be and Al are made passive by HNO<sub>3</sub>.
- Chlorophyll contains Mg and chlorine.
- Chlorophyll produces sugars for the plants in presence of sunlight, CO<sub>2</sub> and H<sub>2</sub>O by photosynthesis.
- Chlorophyll is an organometallic compound.
- The lattice energies of alkaline earth metal salts are much higher than these of alkali metal salts.
- Decreasing lattice energy favours increased solubility, while decreasing hydration energy favours decreased solubility.
- BeO has hexagonal ZnS structure.
- Beryllium forms hydrate peroxide BeO<sub>2</sub> · H<sub>2</sub>O.
- Calcium and barium bicarbonates are stable only in solution and decompose on removal of water to give carbonates.
- Formation of stalactite and stalagmite is the property of calcium and barium bicarbonates which change to carbonates.

### Fill in the Blanks

- ..... of IA and ..... of IIA show diagonal relationship.
- (IE)<sub>1</sub> of Be is ..... than that of B and (IE)<sub>2</sub> of Be is ..... than that of B.
- Of the alkaline earth metals only ..... carbide gives CH<sub>4</sub> on reaction with H<sub>2</sub>O.
- Alkali metal and alkaline earth metal chlorides can be detected by ..... test.
- BeCl<sub>2</sub> is an ..... and has ..... structure in solid state.

6.  $\text{Be}(\text{OH})_2$  is .....
7. Solubility of sulphates and carbonates of alkaline earth metals ..... as the atomic number of the metal increases (down the group).
8.  $\text{BeCO}_3$  is placed in an atmosphere of ..... since, it is .....
9. Be and ..... show diagonal relationship.
10. Be is not readily attacked by acids due to formation of ..... layer.
11. Be dissolves in alkali to give .....
12.  $\text{HCO}_3^-$  is .....
13. Be forms complexes with coordination number .....
14. The thermal stability of group 2 oxysalts is ..... than those of the group 1 oxy salts.
15.  $\text{Ca}(\text{NO}_3)_2$  decomposes into gases ..... and .....
16. .... is the primary constituent of teeth and bones
17. Amphoteric oxide of group 2 is .....
18.  $\text{MgO}$  is used as .....
19.  $\text{Ca}(\text{OH})_2$  is called ..... and  $\text{Ba}(\text{OH})_2$  is called .....
20. Most soluble sulphate of group 2 is .....
21. Potash magnesia is .....
22.  $\text{CaSO}_4 \cdot \text{H}_2\text{O}$  is called ..... and is used to make .....
23.  $\text{BeCl}_2$  fumes in air due to formation of .....
24.  $\text{BeCl}_2$  exists as monomer in ..... state.
25. Polymeric  $\text{BeCl}_2$  has ..... centre ..... electron bonds.

## Matrix-Match Type Questions

### I. Only One Correct

1. Match the commercial names (in List I) with the chemical formulae (in List II).

| List I         | List II                                      |
|----------------|----------------------------------------------|
| A. Magnesite   | 1. $\text{BeO}$                              |
| B. Epsom salt  | 2. $\text{Ca}(\text{OH})_2$                  |
| C. Anhydrite   | 3. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ |
| D. Hydrolith   | 4. $\text{CaH}_2$                            |
| E. Beryllia    | 5. $\text{MgO}$                              |
| F. Slaked lime | 6. $\text{Mg}(\text{ClO}_4)_2$               |

2. Match the mineral names (in List I) with the chemical formulae (in List II).

| List I        | List II                                                       |
|---------------|---------------------------------------------------------------|
| A. Magnesite  | 1. $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ |
| B. Dolomite   | 2. $\text{MgSO}_4 \cdot \text{H}_2\text{O}$                   |
| C. Kieserite  | 3. $\text{MgCO}_3$                                            |
| D. Carnallite | 4. $\text{MgCO}_3 \cdot \text{CaCO}_3$                        |

3. Match compounds (in List I) with the specific properties of the compounds (in List II).

| List I                         | List II                    |
|--------------------------------|----------------------------|
| A. $\text{BeCO}_3$             | 1. Temporary hardness      |
| B. $\text{BaCl}_2$             | 2. Permanent hardness      |
| C. $\text{MgSO}_4$             | 3. Decomposes readily      |
| D. $\text{Ca}(\text{HCO}_3)_2$ | 4. Gives green edged flame |

### II. One or More Correct

1. Match the species in Column I with their corresponding property (ies) in Column II.

| Column I                   | Column II                   |
|----------------------------|-----------------------------|
| A. $\text{BeO}$            | 1. Amphoteric               |
| B. $\text{Al}_2\text{O}_3$ | 2. Diagonal relationship    |
| C. $\text{MgO}$            | 3. Lime water               |
| D. $\text{CaO}$            | 4. Baryta water             |
| E. $\text{BaO}$            | 5. Water insoluble          |
|                            | 6. Maximum soluble in water |
|                            | 7. Estimation by EDTA       |

2. Match the species in Column I with their corresponding property (ies) in Column II.

| Column I | Column II                                                                      |
|----------|--------------------------------------------------------------------------------|
| A. Li    | 1. Diagonal relationship                                                       |
| B. Be    | 2. Maximum standard reduction electrode potential ( $E^\circ$ )                |
| C. Mg    | 3. Cation is maximum hydrated                                                  |
| D. Al    | 4. Cation has maximum ionic mobility in aqueous solution                       |
| E. Ca    | 5. Fluoride and carbonate least soluble in water                               |
|          | 6. Coordination number six in the complexes                                    |
|          | 7. Ions are involved in the transmission of electrical impulses in human body. |

## Integer Answer Types

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the *ORS* have to be darkened. For example, if the correct answers to question number *X, Y, Z* and *W* (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will like the following :

| X | Y | Z | W |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 1 | 1 | 1 | 1 |
| 2 | 2 | 2 | 2 |
| 3 | 3 | 3 | 3 |
| 4 | 4 | 4 | 4 |
| 5 | 5 | 5 | 5 |
| 6 | 6 | 6 | 6 |
| 7 | 7 | 7 | 7 |
| 8 | 8 | 8 | 8 |
| 9 | 9 | 9 | 9 |

## Set 1

1. Coordination number of complexes of beryllium is .....
2. Number of water molecules in gypsum is .....
3. Epsom salt contains ..... water molecules (of hydration)
4. Magnesium allyide is  $\text{Mg}_2\text{C}_x$  where  $x$  is .....
5. Magnesium nitride is  $\text{Mg}_x\text{N}_y$  where  $(x + y)$  is .....
6. Magnesium is coordinated to ..... N atoms in chlorophyll.
7. Bleaching powder has two types of chlorine one with oxidation number  $-1$  and other with oxidation number .....
8. One mole of  $\text{Ca}(\text{HCO}_3)_2$  is neutralised by ..... mole(s) of  $\text{KOH}$ .

## Set II

1. Number of electrons in magnesium ion formed by three steps ionisation of magnesium is .....
2. Number of neutrons in  ${}^9_4\text{Be}^{3+}$  is .....
3. Magnesium is coordinated to N-atoms in chlorophyll. Number of rings in chlorophyll is .....
4. When  $\text{Cl}_2$  is passed into hot alkali solution, products formed have two types of chlorine. Difference in oxidation number of two chlorine atoms is .....

5. 96 g of Mg is burnt in air in a closed chamber. On analysis 25% of Mg is converted into oxide and remaining Mg into other possible product. Residue is dissolving in  $\text{H}_2\text{O}$  and neutralised by  $\text{H}_2\text{SO}_4$ . Number of moles of  $\text{H}_2\text{SO}_4$  required is .....

6.  $E^\circ_{M^{2+}/M}$  values of some metals are

Be : -1.85 V  
Mg : -2.37 V  
Ca : -2.87 V  
Sr : -2.89 V  
Cu : +0.34 V  
Hg : 0.80 V

Number of metals which can displace  $H_2$  gas from acid is .....

7.  $\text{Mg}_x\text{Ba}_y(\text{CO}_3)_z$  has 8.54% Mg, 48.75% Ba and remaining carbonate. 0.281 kg is decomposed by  $\text{H}_2\text{SO}_4$ .  $\text{CO}_2$  formed is ..... mole(s).

8. In question (7),  $x + y + z = \dots\dots\dots$

## Test Yourself on the Periodic Table

1. Identify the elements in the Periodic Table
- A : which shows diagonal relationship to Be
  - B : which shows diagonal relationship to Li
  - C : whose alkali metal carbonate is decomposed on heating
  - D : coinage metals

A large grid of 100 squares arranged in a 10x10 pattern. The grid is composed of 10 rows and 10 columns. The top row has 10 squares. The second row has 9 squares, with the last square missing. The third row has 10 squares. The fourth row has 10 squares. The fifth row has 10 squares. The sixth row has 10 squares. The seventh row has 10 squares. The eighth row has 10 squares. The ninth row has 10 squares. The tenth row has 10 squares. The grid is shaped like a stylized 'E' or a comb, with the top row being the widest and the bottom row being the narrowest.

2. Out of the elements marked A, B, C, D, E, F, G, and H
- which form superoxide?
  - which form thermally stable carbonate?
  - which forms strongest base?
  - which show diagonal relationship?
  - which forms amphoteric oxide?



# Answers & Solutions

## Master Exercises

### Exercise 1

#### Short Answer Type Questions

- Be < Ca < Ba < Ra
  - Ba < Ra < Ca < Be
  - Ba < Ca < Be
  - Ba < Ca < Be ( $\approx 0$ )
- $\text{RaCl}_2 < \text{BaCl}_2 < \text{SrCl}_2 < \text{CaCl}_2 < \text{MgCl}_2 < \text{BeCl}_2$
  - $\text{BeCl}_2 < \text{MgCl}_2 < \text{CaCl}_2 < \text{SrCl}_2 < \text{BaCl}_2 < \text{RaCl}_2$
  - $\text{RaCl}_2 < \text{BaCl}_2 < \text{SrCl}_2 < \text{CaCl}_2 < \text{MgCl}_2 < \text{BeCl}_2$   
(numerical value)
  - $\text{RaCl}_2 < \text{BaCl}_2 < \text{SrCl}_2 < \text{CaCl}_2 < \text{MgCl}_2 < \text{BeCl}_2$
- $\text{Ca}(\text{HCO}_3)_2 < \text{NaHCO}_3$
  - $\text{CaCO}_3 < \text{Na}_2\text{CO}_3$
  - $\text{BeCO}_3 < \text{Li}_2\text{CO}_3$
  - $\text{NaHCO}_3 < \text{Na}_2\text{CO}_3$
- $$\text{Mg} + \frac{1}{2} \text{O}_2 \longrightarrow \text{MgO}$$

$$3\text{Mg} + \text{N}_2 \longrightarrow \text{Mg}_3\text{N}_2$$
- Barium carbonate due to very high lattice energy decomposes at about  $1400^\circ\text{C}$ 

$$\text{BaCO}_3 \longrightarrow \text{BaO} + \text{CO}_2$$

At such high temperature, the reaction tends to become reversible. Carbon added combines with  $\text{CO}_2$  forming CO and thus reaction is made irreversible.

$$\text{CO}_2 + \text{C} \longrightarrow 2\text{CO}$$
- If strongly ignited magnesium oxide is added to a concentrated solution magnesium chloride, the slurry so obtained solidifies in the course of a few hours, to a solid mass. This is called **sorel cement** or **magnesia cement**.

When mixed with saw-dust or cork waste, sorel cement gives a weather proof composition.

#### Analytical Questions

- Chlorophyll
- Hydrated cation is  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ .  

$$[\text{Be}(\text{H}_2\text{O})_4]^{2+} + \text{H}_2\text{O} \longrightarrow [\text{Be}(\text{H}_2\text{O})_3(\text{OH})]^+ + \text{H}_3\text{O}^+$$
hydrated cation is  $\text{H}^+$  ion donor, hence, it behaves as an acid (Lowry-Bronsted protonic concept).
- This indicates that concentration of NaOH is very high hence, pH is greater than 14.
- $\text{BeCl}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Be}(\text{OH})_2 + 2\text{HCl}$   
HCl causes fumes formation.
- (a) See text (b) See text (c) See text
- (A) :  $\text{BaO}_2$  (B) :  $\text{BaSO}_4$  (C) :  $\text{H}_2\text{O}_2$  (D) : Refer text
- (a) Refer text (b) Refer text (c) Refer text (d) Refer text
- $$\text{Na}_2\text{CO}_3 \xrightarrow{\Delta} \text{no effect}$$

$$\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$$
  - $$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \xrightarrow{\Delta} \text{Mg}(\text{OH})\text{Cl} \cdot 5\text{H}_2\text{O} + \text{HCl}$$

$$\text{CaCl}_2 \cdot 6\text{H}_2\text{O} \xrightarrow{\Delta} \text{CaCl}_2 + 6\text{H}_2\text{O}$$
  - $$2\text{Ca}(\text{NO}_3)_2 \xrightarrow{\Delta} 2\text{CaO} + 2\text{NO}_2 + 3\text{O}_2$$

$$2\text{NaNO}_3 \xrightarrow{\Delta} 2\text{NaNO}_2 + \text{O}_2$$

#### NCERT Problems

Refer Text

### Exercise 2

#### Only One Option Correct

- |         |         |         |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (a)  | 2. (c)  | 3. (d)  | 4. (c)  | 5. (d)  | 6. (b)  | 7. (b)  | 8. (c)  | 9. (c)  | 10. (a) |
| 11. (a) | 12. (d) | 13. (c) | 14. (d) | 15. (c) | 16. (d) | 17. (d) | 18. (b) | 19. (a) | 20. (a) |
| 21. (a) | 22. (b) | 23. (a) | 24. (c) | 25. (a) | 26. (d) | 27. (b) | 28. (d) | 29. (d) | 30. (c) |
| 31. (c) | 32. (a) | 33. (d) | 34. (a) | 35. (d) | 36. (d) | 37. (b) | 38. (b) | 39. (d) | 40. (d) |
| 41. (d) | 42. (c) | 43. (d) | 44. (a) | 45. (d) | 46. (a) | 47. (a) | 48. (a) | 49. (b) | 50. (c) |
| 51. (c) | 52. (c) | 53. (d) | 54. (b) | 55. (a) | 56. (a) | 57. (b) | 58. (b) | 59. (c) | 60. (c) |
| 61. (d) | 62. (c) | 63. (a) | 64. (c) | 65. (b) | 66. (a) | 67. (d) | 68. (a) | 69. (c) | 70. (c) |
| 71. (c) | 72. (d) | 73. (b) | 74. (d) | 75. (a) | 76. (c) | 77. (c) | 78. (c) | 79. (a) | 80. (d) |
| 81. (a) | 82. (c) | 83. (d) |         |         |         |         |         |         |         |

## Brain Twisters

1. If the reaction is to be product-favoured, i.e., it is spontaneous in forward side then  $\Delta G^\circ$  should be negative and  $\Delta G^\circ$  for  $MX_n$  should be greater than and more negative than  $(95.1) \times n$  kJ.

2. 24 L of  $\text{CO}_2$  at 298 K and 1 atm = 1 mol  $\text{CO}_2$

$$48 \text{ mL} (=0.048 \text{ L}) = \frac{1}{24} \times 0.048$$

$$= 0.002 \text{ mol } \text{CO}_2 \text{ in } 100 \text{ mL solution}$$

$$= 0.02 \text{ M}$$

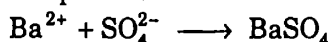
EDTA complexes with  $\text{Mg}^{2+}$  and  $\text{Ba}^{2+}$

$$M_1 V_1 = M_2 V_2$$

$$M_1(\text{Mg}^{2+} \text{ and } \text{Ba}^{2+}) \times 25 = 25 \times 0.02$$

$$= 0.02 \text{ M} = 0.02 \text{ mol L}^{-1}$$

$$M_1(\text{Mg}^{2+}) + M_1(\text{Ba}^{2+}) = 0.02 \text{ M}$$



$$137 \text{ g} = 1 \text{ mol} \quad 233 \text{ g} = 1 \text{ mol}$$

$$233 \text{ g } \text{BaSO}_4 \text{ is from } = 137 \text{ g } \text{Ba}^{2+} = 1 \text{ mol } \text{Ba}^{2+}$$

$$\therefore 0.058 \text{ g } \text{BaSO}_4 \text{ is from } = \frac{0.058}{233} = 2.5 \times 10^{-4} \text{ mol } \text{Ba}^{2+}$$

in 25 mL

$$\therefore [\text{Ba}^{2+}] = 0.01 \text{ mol L}^{-1}$$

$$\therefore [\text{Mg}^{2+}] = 0.01 \text{ mol L}^{-1}$$

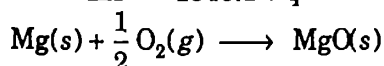
Thus,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{CO}_3^{2-}$  are in molar ratio of 1 : 1 : 2

$\therefore$  Salt is  $\text{MgBa}(\text{CO}_3)_2$

3. Stepwise formation of  $\text{MgO}$  involves

| Step  | Reaction                                                                           | $\Delta H$ kJ mol <sup>-1</sup> |
|-------|------------------------------------------------------------------------------------|---------------------------------|
| I     | $\text{Mg(s)} \longrightarrow \text{Mg(g)}$                                        | 147.7                           |
| II    | $\text{Mg(g)} \longrightarrow \text{Mg}^{2+}(\text{g}) + 2\text{e}^-$              | 2189.0                          |
| III   | $\frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{O(g)}$                     | $\frac{498.4}{2}$               |
| IV    | $\text{O(g)} + \text{e}^- \longrightarrow \text{O}^-(\text{g})$                    | -141.0                          |
| V     | $\text{O}^-(\text{g}) + \text{e}^- \longrightarrow \text{O}^{2-}(\text{g})$        | $q$                             |
| VI    | $\text{Mg}^{2+}(\text{g}) + \text{O}^{2-}(\text{g}) \longrightarrow \text{MgO(s)}$ | -3791.0                         |
| <hr/> |                                                                                    |                                 |
|       | $\text{Mg(s)} + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{MgO(s)}$    |                                 |

$$\Delta H = -1346.1 + q$$



$$\Delta H_2 = -601.7$$

By Born-Haber Cycle (based on Hess law)

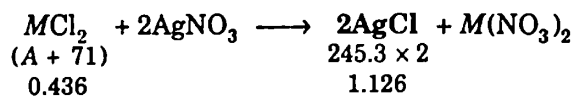
$$\Delta H_1 = \Delta H_2$$

$$-1346.1 + q = -601.7$$

$$q = 744.4 \text{ kJ mol}^{-1}$$

4. Let molar mass of the element ( $M$ ) =  $A$

$$\text{Moles of element} = \frac{1.005}{A}$$



$$\frac{A + 71}{0.436} = \frac{243.5 \times 2}{1.9126}$$

$$\therefore A = 40 \text{ g mol}^{-1}$$

(a) Thus element is **Ca**

(b) Molar mass of  $\text{CaCl}_2 = 111 \text{ g mol}^{-1}$

$$\% \text{ of Cl} = \frac{71}{111} \times 100$$

$$= 63.96\%$$

## Passage Comprehension Questions

## Passage 1

1. (b) 2. (d) 3. (a)

## Passage 2

1. (b) 2. (a)

## Passage 3

1. (c) 2. (a) 3. (b) 4. (d)

## Passage 4

1. (a) 2. (b) 3. (c)

## Assertion &amp; Reason

1. (a) 2. (b) 3. (a) 4. (a) 5. (b)

## True &amp; False

1. T 2. T 3. T 4. F (decreases)  
 5. F (propyne) 6. T 7. T  
 8. F (due to  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ )  
 9. F ( $\text{BeCl}_2$  is an electrophile)  
 10. T 11. T 12. F 13. T  
 14. F (Mg is coordinated to N)  
 15. T 16. T 17. T 18. F 19. T 20. T

## Fill in the Blanks

1. Li, Mg 2. higher, smaller 3. beryllium  
 4. flame 5. electrophile, polymeric 6. amphoteric  
 7. decreases 8.  $\text{CO}_2$ , thermally unstable 9. Al  
 10. oxide 11.  $\text{Na}_2\text{BeO}_2$  and  $\text{H}_2$  12. amphoteric  
 13. four 14. less 15.  $\text{NO}_2$ ,  $\text{O}_2$  16.  $\text{Ca}_3(\text{PO}_4)_2$   
 17. BeO 18. refractory 19. lime water, baryta water  
 20.  $\text{BeSO}_4$  21.  $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$   
 22. Alabaster, ornaments 23. HCl 24. vapour  
 25. three, two

### Matrix-Match Type Questions

### I. Only One Correct

1. (A)—(5); (B)—(3); (C)—(6); (D)—(4);  
(E)—(1); (F)—(2);
2. (A)—(3); (B)—(4); (C)—(2); (D)—(1)
3. (A)—(3); (B)—(4); (C)—(2); (D)—(1)

## II. One or More Correct

1. (A)—(1,2,5); (B)—(1,2,5); (C)—(2,7);  
(D)—(3,7); (E)—(4,6)
2. (A)—(1,2,); (B)—(1,3); (C)—(1,6,7);  
(D)—(1,6); (E)—(4,5,6,7)

## Integer Answer Types

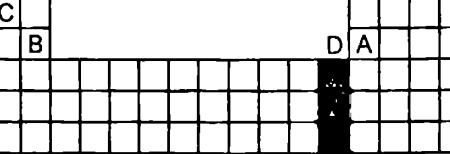
## Set I

|             |   |   |   |   |   |   |   |   |
|-------------|---|---|---|---|---|---|---|---|
| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Answers →   | 4 | 2 | 7 | 3 | 5 | 4 | 1 | 2 |
|             | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
|             | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|             | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
|             | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
|             | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
|             | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
|             | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
|             | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
|             | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
|             | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |

## Set II

|             |   |   |   |   |   |   |   |   |
|-------------|---|---|---|---|---|---|---|---|
| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Answers →   | 9 | 5 | 8 | 8 | 5 | 4 | 2 | 4 |
|             | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
|             | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|             | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
|             | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
|             | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
|             | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
|             | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
|             | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
|             | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
|             | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |

## Test Yourself on the Periodic Table

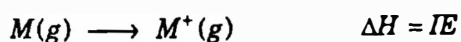
1. 
2. (a) E and G (b) C, E, and G (c) G  
(d) A and D (e) B

The science fiction writer Jules Verne had an uncanny knack of predicting the future. In 1874, he wrote "I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light" Many now believe that this prophecy has come true in the twenty-first century when a major research work is being carried out with hydrogen and it may become a universal fuel.

# Hydrogen and Its Compounds

## Quick Points

- Ionisation Energy is the energy required to convert gaseous atom to gaseous ion, i.e.,



- Electronegativity is measured in Pauling scale (w.r.t. H)
- Entropy is the measure of the disorder of the system

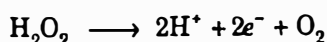
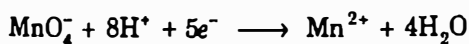
$$\Delta S = \frac{q}{T}$$

- Ionic product of  $H_2O$ ,  $K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$  at 298 K

Ionisation constant of a weak acid HA (with ionisation step  $HA + H_2O \longrightarrow H_3O^+ + A^-$ ) is

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- In an electrochemical cell, oxidation takes place at anode and reduction takes place at cathode.
- $MnO_4^-$  is used to determine concentration of  $H_2O_2$  volumetrically



- 1 mol of every gas at STP occupies volume 22.4 L or 22400 mL or  $0.0224 \text{ m}^3$
- Molarity is the concentration in  $\text{mol L}^{-1}$
- Normality is the concentration in equivalent  $\text{L}^{-1}$

## Learning Framework of the Chapter

- Hydrogen
- Hydrogen Peroxide

In many ways, hydrogen is unique and although it is hardly found on earth as the free element, life here would be impossible without it (Fig. 10.1). It accounts for virtually all of our energy, either directly in the form of sunlight, or indirectly as fossil fuels. Without hydrogen there would be no water to drink and DNA molecules would not form the double-helix structure that allows our genetic code to be copied and passed on to future generations.

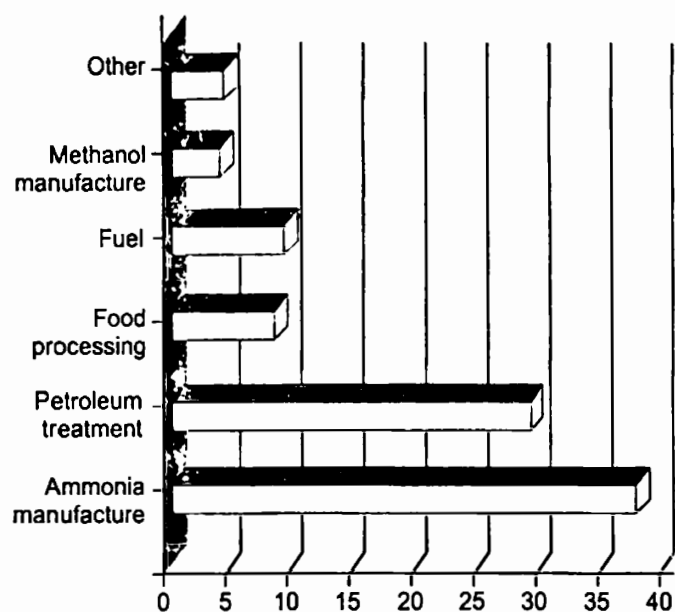


Fig. 10.1 Some of the most important industrial uses of hydrogen

### DEEP Focus

Hydrogen is the most abundant lightest element in the universe and oxygen is the most abundant element on the earth's surface. In the earth's crust and oceans, **hydrogen is the ninth most abundant element on a mass basis (0.9%) and the third most abundant on an atom basis (15.4 atom %)**. Hydrogen combines with every element in the Periodic Table except the noble gases and forms more compounds than any other element.

Henry Cavendish, an English chemist and physicist, was the first person to isolate hydrogen in pure form (but did not name it) by action of dilute acids such as HCl, H<sub>2</sub>SO<sub>4</sub> on metals such as Zn, Sn, etc.



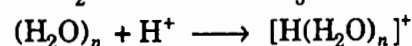
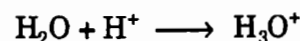
The French chemist Lavoisier called the gas "hydrogen" meaning "water former" because it combines with oxygen to produce water.

## Hydrogen

### Electronic Structure (1s<sup>1</sup>)

Hydrogen has the simplest atomic structure of all the elements, and consists of a nucleus containing one proton with a charge +1 and one orbital electron (1s<sup>1</sup>). Atoms of hydrogen may attain stability in three different ways :

- by forming an electron pair (covalent) bond with another atom as in H<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>, HCl, CH<sub>4</sub>
- by losing an electron to form H<sup>+</sup>; a proton is of approximately 1.5 × 10<sup>-5</sup> Å radius compared to that of H which is 0.7414 Å. Due to its very small size, H<sup>+</sup> has a very high polarising power, and therefore distorts the electron cloud on other atoms. H<sup>+</sup> (protons) is always associated with other atoms or molecules, as H<sub>3</sub>O<sup>+</sup>, H<sub>9</sub>O<sub>4</sub><sup>+</sup> or H(H<sub>2</sub>O)<sub>n</sub><sup>+</sup> ions.

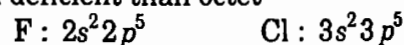


**Free protons do not exist under normal conditions though they are found in low pressure gaseous beams (as in spectrometer)**

- by gaining an electron to form H<sup>-</sup>; crystalline solid such as LiH contains the H<sup>-</sup> ion and are formed by highly electropositive metals (as groups I, II).

### Position in the Periodic Table

- Hydrogen is the first element in the Periodic Table. Hydrogen is placed in no specific group due to its property of gaining electron (when H<sup>-</sup> is formed) and also losing electron (when H<sup>+</sup> is formed).
- Hydrogen is placed in Group I (alkali metals) as :
  - it has one electron in its (outer) shell—1s<sup>1</sup> like other alkali metals which have [inert gas] ns<sup>1</sup> configuration
  - it forms monovalent H<sup>+</sup> ion like Li<sup>+</sup>, Na<sup>+</sup>, ....
  - its valency is also 1
  - its oxide (H<sub>2</sub>O) is stable as Li<sub>2</sub>O, Na<sub>2</sub>O
  - it is a good reducing agent (in atomic as well as molecular state) like Na, Li, ....
- Hydrogen also resembles halogens (Group 17) as :
  - it is also diatomic (H<sub>2</sub>) like F<sub>2</sub>, Cl<sub>2</sub>, ....
  - it also forms anion H<sup>-</sup> like F<sup>-</sup>, Cl<sup>-</sup>, .... by gain of one electron
  - H<sup>-</sup> has stable inert gas [He] configuration as F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> have
  - it forms covalent compounds with carbon as CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> like halogens CCl<sub>4</sub>, CF<sub>2</sub>Cl<sub>2</sub> etc.
  - H is one electron short of duplet (stable configuration) like F, Cl, ... which are also one electron deficient than octet



- (IE) of H(1312 kJ mol<sup>-1</sup>) is of the same order as that of halogens, as :

| Atom | (IE), kJ mol <sup>-1</sup> |
|------|----------------------------|
| H    | 1312                       |
| F    | 1681                       |
| Cl   | 1256                       |
| Br   | 1143                       |
| I    | 1009                       |

- (IE) of H is very high in comparison with alkali metals. Also size of  $H^+$  is very small compared to that of alkali metal ions. H forms stable hydride only with strongly electropositive metals due to smaller value of its electron affinity ( $72.8 \text{ kJ mol}^{-1}$ ).
- In view of the anomalous behaviour of hydrogen, it is difficult to assign any definite position to it in the Periodic Table. Hence, it is customary to place it in Group I (along with alkali metals) as well as in Group (17) VIIA (along with halogens).

| 1(IA) | 17(VIIA) |
|-------|----------|
| H     | H        |
| Li    | F        |
| Na    | Cl       |
| K     | Br       |
| Rb    | I        |
| Cs    | At       |
| Fr    |          |

Table 10.1 A Comparison of Some Properties of Hydrogen, Lithium, Carbon and Fluorine

| Property                                      | Hydrogen           | Lithium<br>(Group 1) | Carbon<br>(Group 14)    | Fluorine<br>(Group 17)  |
|-----------------------------------------------|--------------------|----------------------|-------------------------|-------------------------|
| Electron configuration                        | $1s^1$             | $[\text{He}] 2s^1$   | $[\text{He}] 2s^2 2p^2$ | $[\text{He}] 2s^2 2p^5$ |
| First ionization energy/ $\text{kJ mol}^{-1}$ | +1312              | +519                 | +1090                   | +1681                   |
| Electron affinity/ $\text{kJ mol}^{-1}$       | -72                | -52                  | -120                    | -348                    |
| Electronegativity (Pauling)                   | 2.1                | 1.0                  | 2.5                     | 4.0                     |
| Structure                                     | diatomic molecules | metallic lattice     | covalent macromolecule  | diatomic molecule       |
| Atomization energy/ $\text{kJ mol}^{-1}$      | +218               | +161                 | +715                    | +79                     |

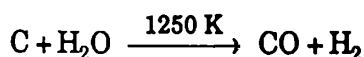
## Manufacture of Hydrogen

- Water is the natural abundant source for the manufacture of hydrogen.

Reduction of water of hydrogen can be carried out.

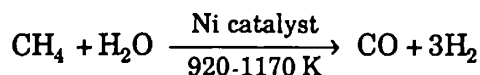
(1) Chemically (2) Electrolytically common reducing agents are (1) Coke (2) Carbon monoxide (3) Hydrocarbons

(1) Hydrogen is manufactured by allowing steam to react with red hot coke at about  $1250 \text{ K}$ .

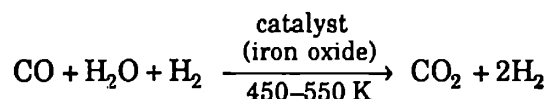


This mixture of CO and  $\text{H}_2$  is also known as **water gas** and the reaction is referred to as **water gas reaction**. As this mixture ( $\text{CO} + \text{H}_2$ ) is used for the synthesis of methanol and a number of hydrocarbons, this is also called **synthesis gas**.

(2) Hydrogen is now produced by the reaction of natural gas (chiefly methane) with steam in presence of a nickel catalyst.



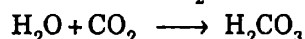
Similar reaction can occur with other hydrocarbons also. In both the above processes CO is converted to  $\text{CO}_2$  and more hydrogen generated by passing the gases ( $\text{CO} + \text{H}_2$ ) and steam over iron oxide or cobalt oxide catalyst.



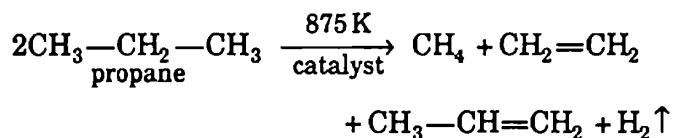
This reaction is called **water gas shift reaction**

## DEEP Focus

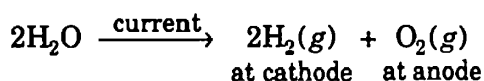
Hydrogen and carbon dioxide can be easily separated from each other by bubbling the gas mixture through water in which  $\text{CO}_2$  is fairly soluble and  $\text{H}_2$  virtually insoluble.



(3) At higher temperature, in the presence of catalysts (silica, alumina) hydrocarbons decompose and rearrange in what are called **cracking reactions**. These reactions, which are used in refining of petroleum, produce hydrogen as a by-product.



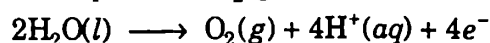
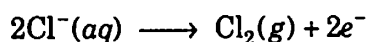
(4) **Electrolysis of acidified water using platinum electrodes.** On a large scale, very pure hydrogen (> 99.95%) can be obtained from the electrolysis of aqueous solutions of barium hydroxide between nickel electrodes.



Hydrogen is economically obtained as a by-product in the electrolysis of brine solution in the manufacture of sodium hydroxide.

**At anode :**

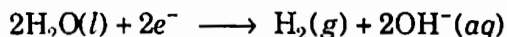
During electrolysis there is a **competition** at the anode between the oxidation of chloride ion and the oxidation of water.



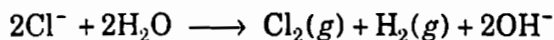
When a concentrated salt solution (brine) is used, the first reaction is the one that is observed.

**At cathode :**

The reaction is the reduction of water because it is more easily reduced than  $\text{Na}^+$



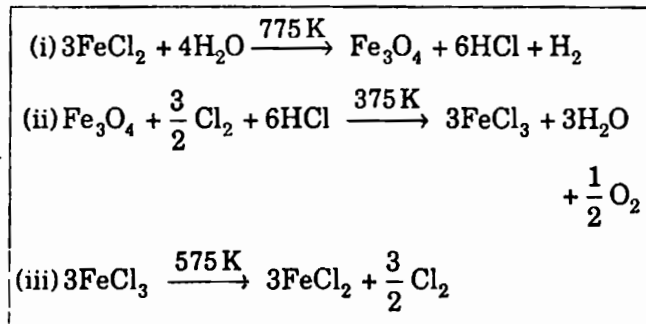
**Overall reaction is**



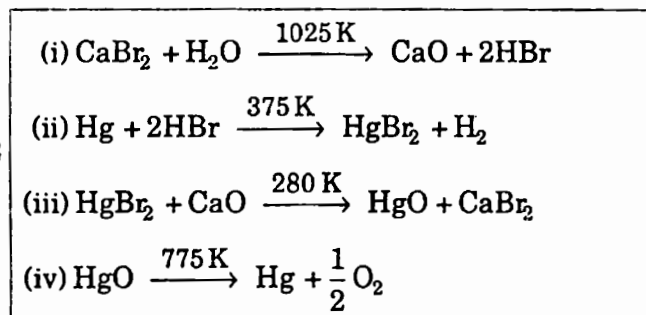
Water is very stable to thermal decomposition, it does not decompose to hydrogen and oxygen to any appreciable extent at practically viable temperatures. Great efforts are being made to make electrolysis of water more energy-efficient so that the use of hydrogen as a fuel can become economically viable.

**(5) Non-electrolytic methods of preparation of hydrogen, e.g., thermochemical and photochemical.** In thermochemical hydrogen generation, water is heated with certain chemicals to liberate hydrogen at much lower temperatures. Two potentially useful cycles are given below :

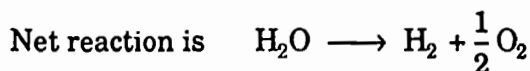
**Cycle 1**



**Cycle 2**



Thus, by repeating reactions (i)–(iii) in cycle 1 or reactions (i)–(iv) in cycle 2, water can be splitting to  $\text{H}_2$  and  $\text{O}_2$ .



Decomposition of water by solar energy in presence of catalyst is known as **photochemical decomposition of water**. Using special catalysts, scientists in France have been able to achieve the efficient decomposition of water under visible and ultraviolet light.

## Properties

- Some of the physical properties of hydrogen atoms are summarised in Table 10.2.

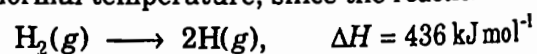
**Table 10.2 Physical Properties of Hydrogen**

|                                                         |                                      |
|---------------------------------------------------------|--------------------------------------|
| Relative atomic mass                                    | 1.008                                |
| Electron structure                                      | $1s^1$                               |
| (IE), $\text{H}(g) \longrightarrow \text{H}^+(g) + e^-$ | $1312\text{ kJ mol}^{-1}$            |
| Electronegativity (Pauling scale)                       | 2.1                                  |
| Electron affinity                                       | $-72\text{ kJ mol}^{-1}$             |
| Molecular formula                                       | $\text{H}_2$                         |
| Melting point                                           | $-259^\circ\text{C}$                 |
| Boiling point                                           | $-253^\circ\text{C}$                 |
| Density at STP                                          | $0.09\text{ g L}^{-1}$               |
| B.E. (H—H)                                              | $436\text{ kJ mol}^{-1}$             |
| Bond length (H—H)                                       | 74 pm                                |
| Covalent radius                                         | 37 pm                                |
| van der Waals' radius                                   | 120 pm                               |
| Ionic radius ( $\text{H}^-$ )                           | 208 pm                               |
| Standard entropy                                        | $131\text{ JK}^{-1}\text{ mol}^{-1}$ |
| Heat capacity ( $25^\circ\text{C}$ )                    | $297\text{ JK}^{-1}\text{ mol}^{-1}$ |

- At ordinary temperatures and pressures, hydrogen is a colourless, odourless and tasteless gas composed of diatomic  $\text{H}_2$  molecules. Because  $\text{H}_2$  is a non-polar molecule that contains only two electrons, **intermolecular forces are very weak** hence, it (in the solid form it has hexagonal close-packed structure) has very low melting point ( $-259^\circ\text{C}$ ) and low boiling point ( $-253^\circ\text{C}$ ). The bonding forces within the  $\text{H}_2$  molecule are exceptionally strong and  $\text{H}_2$  molecule is thus, thermally stable. Even at 2000 K, only 1 of every 2500  $\text{H}_2$  molecules is dissociated into H-atoms.

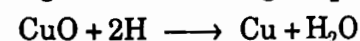
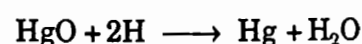
## Atomic Hydrogen

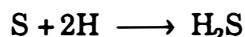
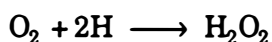
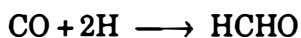
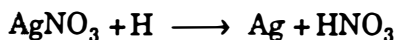
Hydrogen is the lightest element known. It is a colourless, odourless and tasteless gas. Hydrogen molecule is thermally stable and has little tendency to dissociate at normal temperature, since the reaction.



is highly endothermic. However, at high temperatures in an electric arc or under ultraviolet light, it does dissociate. The **atomic hydrogen** produced, exists for less than half a second, after which it recombines to give molecular hydrogen and liberates a large amount of energy ( $436\text{ kJ mol}^{-1}$ ) in the form of heat. Most of the transition metals catalyse the recombination reaction of atomic hydrogen.

Atomic hydrogen is a powerful **reducing agent** and reduces copper, silver and mercury salts to the metallic state. It combines with alkali metals to form hydrides, reduces sulphur to hydrogen sulphide and carbon monoxide to formaldehyde. It also reacts with oxygen at room temperature to form hydrogen peroxide. The reactions can be written as :





Atomic hydrogen is generally produced by passing ordinary hydrogen through an electric arc maintained between two tungsten electrodes. The atoms set free are carried away by a stream of incoming hydrogen gas. These free atoms recombine at once on coming in contact with a metallic surface liberating a large amount of heat and thus raising the temperature of the metal very high, say to 4000–5000 K. This principle is utilised in making of the 'atomic hydrogen welding torch' (Fig. 10.2). It provides an opportunity of welding at a very high temperature but in a reducing atmosphere.

Despite fairly high bond dissociation energy of hydrogen molecule, it is moderately reactive because hydrogen forms strong bonds with many other elements. It reacts with almost all elements except the noble gases.

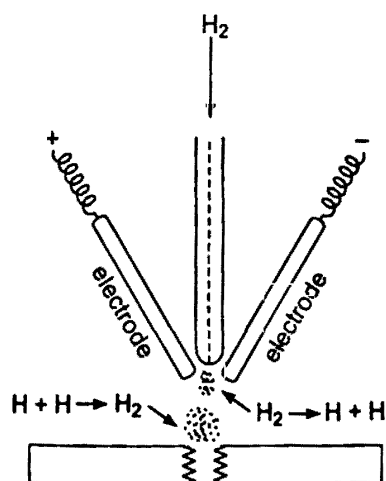
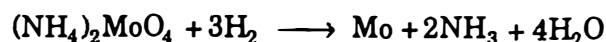
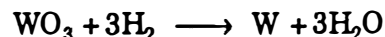


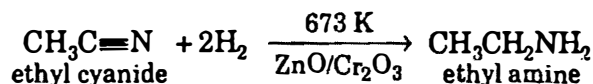
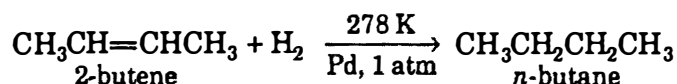
Fig. 10.2 Atomic hydrogen welding torch

## Reducing Agent

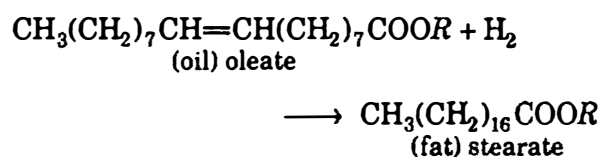
Hydrogen is easily oxidised to water and; therefore, it acts as a very good **reducing agent** in a variety of situations. Hydrogen is used in metallurgy to reduce metal oxides to metals in cases where carbon cannot be used because the metal, e.g., Mo and W can form a carbide :



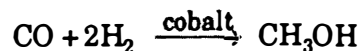
- Hydrogen adds on the **multiple bonds** in organic compounds. In the presence of catalysts such as finely divided nickel, palladium or mixtures of metal oxides, unsaturated organic compounds are thus reduced to saturated compounds.



- Catalytic hydrogenation of unsaturated liquid vegetable oils to solid edible fats.**



- Hydrogen reacts with carbon monoxide in the presence of catalysts to form methanol :



This reaction is known as **hydroformylation** reaction and is used in industrial preparation of methanol.

## Isotopes of Hydrogen

Hydrogen has three isotopes :

| Name      | Symbol                      | Atomic mass | P | N | Percentage          | Nuclear stability | Nuclear spin quantum number | Relative atomic mass |
|-----------|-----------------------------|-------------|---|---|---------------------|-------------------|-----------------------------|----------------------|
| Protium   | ${}_1\text{H}^1$            | 1           | 1 | 0 | 99.986              | Stable            | $\frac{1}{2}$               | 1.007825             |
| Deuterium | ${}_1\text{H}^2 (\text{D})$ | 2           | 1 | 1 | 0.014               | Stable            | 1                           | 2.014102             |
| Tritium   | ${}_1\text{H}^3 (\text{T})$ | 3           | 1 | 2 | $7 \times 10^{-16}$ | Radioactive       | $\frac{1}{2}$               | 3.106049             |

- Physical properties of  $\text{H}_2$ ,  $\text{D}_2$  and  $\text{T}_2$  are summarised in Table 10.3. These isotopes have same electronic configuration and therefore their chemical properties are almost the same. The only difference is in the rate of reaction. Hydrogen has lower energy of activation than deuterium in its reaction with halogen hence, reacts faster.

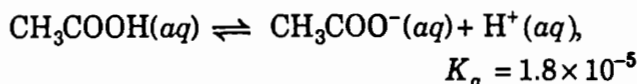


Table 10.3 Physical Properties of Isotopes of Hydrogen

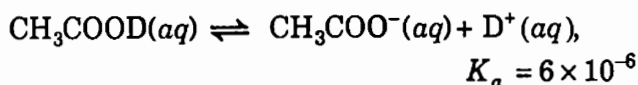
| Physical contents                       | H <sub>2</sub>             | D <sub>2</sub>             | T <sub>2</sub>             |
|-----------------------------------------|----------------------------|----------------------------|----------------------------|
| Freezing point                          | - 259°C                    | - 254.3°C                  | - 252.4°C                  |
| Boiling point                           | - 252.6°C                  | - 249.3°C                  | - 248.0°C                  |
| T <sub>c</sub> (critical temperature)   | -239.8°C                   | - 234.6°C                  | - 232.4°C                  |
| Bond length (H—H)                       | 74 pm                      | 74 pm                      | 74 pm                      |
| BE (H—H)                                | 436.0 kJ mol <sup>-1</sup> | 443.3 kJ mol <sup>-1</sup> | 446.9 kJ mol <sup>-1</sup> |
| Latent heat of vaporisation             | 0.904 kJ mol <sup>-1</sup> | 1.226 kJ mol <sup>-1</sup> | 1.393 kJ mol <sup>-1</sup> |
| Latent heat of fusion                   | 0.117 kJ mol <sup>-1</sup> | 0.197 kJ mol <sup>-1</sup> | 0.250 kJ mol <sup>-1</sup> |
| <b>Water</b>                            | <b>H<sub>2</sub>O</b>      | <b>D<sub>2</sub>O</b>      | <b>T<sub>2</sub>O</b>      |
| Melting point                           | 0.00°C                     | 3.81°C                     | 4.48°C                     |
| Boiling point                           | 100.0°C                    | 101.42°C                   | 101.51°C                   |
| Density at 25°C                         | 0.997 g/cm <sup>3</sup>    | 1.104 g/cm <sup>3</sup>    | 1.214 g/cm <sup>3</sup>    |
| Dissociation constant (K <sub>w</sub> ) | 1.01 × 10 <sup>-14</sup>   | 0.195 × 10 <sup>-14</sup>  | 0.06 × 10 <sup>-14</sup>   |
| Temperature of maximum density          | 4°C                        | 11.6°C                     | —                          |

### DEEP Focus

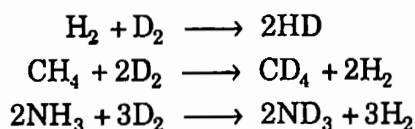
Although, D<sub>2</sub>O chemically resembles H<sub>2</sub>O in many respects, it is toxic substance. The reason is that deuterium is heavier than hydrogen; thus, its compounds often react more slowly than those of the lighter isotope. Regular drinking of D<sub>2</sub>O instead of H<sub>2</sub>O could prove fatal because of the slower rate of transfer of D<sup>+</sup> compared with that of H<sup>+</sup> in the acid-base reactions involved in enzyme catalysis. This **kinetic isotopic effect** is also observed in the ionisation of an acid. Ionisation constant of acetic acid.



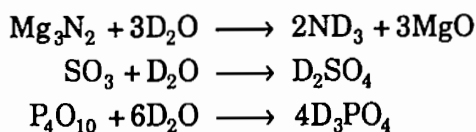
is about three times as large as that of deuterated acetic acid:



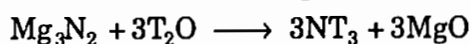
Deuterium undergoes exchange reactions, replacing protium.



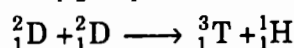
To prepare deuterium rich compounds, heavy water (D<sub>2</sub>O) is used



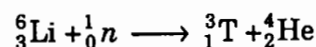
(If T<sub>2</sub>O is used, tritium rich compounds are formed)



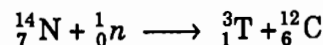
Tritium differs from the other two isotopes of hydrogen in being radioactive. It was first obtained synthetically by the bombardment of deuterium compounds such as (ND<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> with fast deuterons



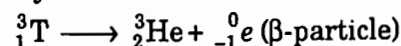
It is now prepared on a large scale by attack of slow neutrons on isotopes of lithium-6



Following reaction also occurs in nature



Tritium disintegrates emitting β-particle, half-life period being 12.3 years.



### DEEP Focus

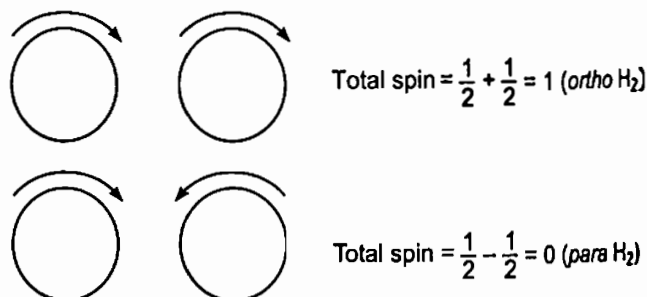
Tritium can be easily incorporated into biological molecules because it behaves chemically, just like ordinary hydrogen. The radiation that tritium gives off within an organism, as a result of its decay, can cause many diseases as cancer.

Tritium is non-toxic, except when inhaled in large quantities.

### Ortho and Para Hydrogen

- In the H<sub>2</sub> molecule, the two nuclei may be spinning in either the same direction or in opposite direction. This gives rise to **spin isomerism**, that is, two different forms of hydrogen may exist :

- if two nuclei have same spin then it is called **ortho** H<sub>2</sub>
- if two nuclei have different spins then it is called **para** H<sub>2</sub>.



- There are considerable differences in physical properties of the *ortho* and *para*  $H_2$  because of differences in their internal energy. *Para*  $H_2$  has a lower internal energy than the *ortho*  $H_2$ .

Hydrogen gas is an equilibrium mixture of *ortho* and *para* hydrogen. The ratio of *ortho* to *para* hydrogen varies with temperature as shown in Fig. 10.3

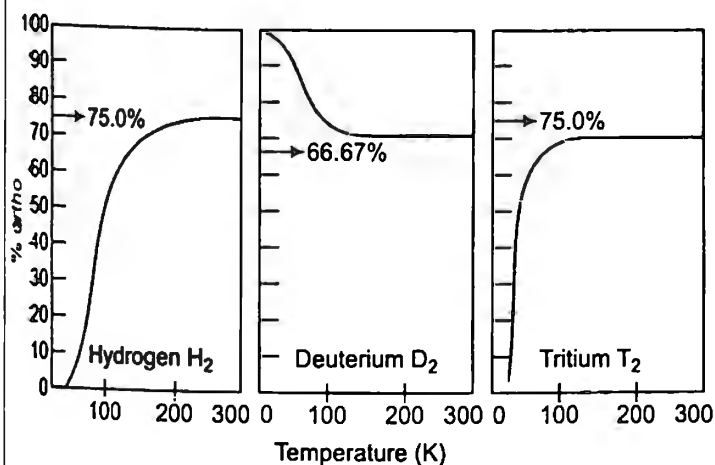


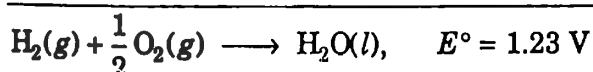
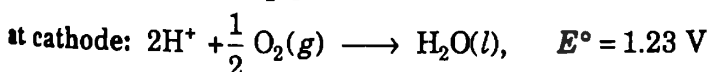
Fig. 10.3 *Ortho-para* equilibria for  $H_2$ ,  $D_2$  and  $T_2$ .

Evidently, this ratio increases with the rise in temperature upto a temperature of about 300 K (27°C) and remains constant thereafter. The percentage of *ortho* hydrogen at 300 K and above is 75%. This means that it is not possible to get 100% *ortho* hydrogen at any temperature. The equilibrium mixture of *para* and *ortho* hydrogen changes to almost 100% *para* hydrogen when cooled nearly to absolute zero. *Para* hydrogen is stable for weeks in the absence of catalysts like activated charcoal, Fe, Ni, Pt,  $O_2$ ,  $NO_2$ , etc., which catalyse the conversion of *para* to *ortho* hydrogen. Similarly, deuterium and tritium also exhibit spin isomerism and exist in *ortho* and *para* forms. However, the ratio of *ortho* and *para* forms in deuterium and tritium is different from that in hydrogen. The variation of *ortho/para* ratio at different temperatures is also different. From Fig. 10.3 it is evident that tritium resembles hydrogen more closely than deuterium in this respect.

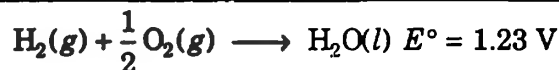
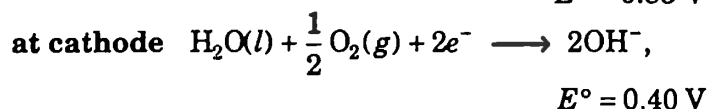
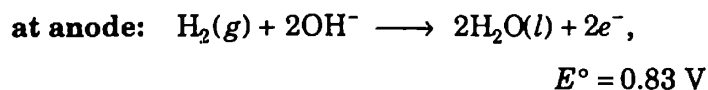
### DEEP Focus

- In spacecrafts,  $H_2$  gas is used in fuel cells for generating electrical energy and for providing clean drinking water to the astronauts. In fuel cell, electrical energy is generated by the reaction of  $H_2$  and  $O_2$  without evolution of any heat: called "cold combustion". A  $H_2-O_2$  fuel cell may have an alkaline or acidic electrolyte.

With acidic electrolyte, the half-cell reactions are:

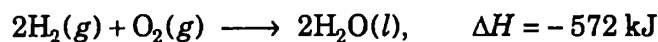


With alkaline electrolyte, the half-cell reactions are:



Thus,  $E^\circ$  is 1.23 V irrespective of the electrolyte because we are using the same reactants ( $H_2$  and  $O_2$ ) at the electrodes. Fuel-cells have greater efficiency (about 75%) than other rechargeable secondary cells (about 40%)

Combustion of hydrogen is a highly exothermic reaction and produces no pollutants:



Liquid hydrogen is, therefore, used as a **rocket fuel**.

It has been recognised during the past two decades that the world reserves of fossil fuels like coal, oil and gas are finite, so they cannot last for ever. Similarly, the nuclear and hydroelectric power also cannot meet all our energy requirements. Moreover, these sources pose a danger of environmental degradation. This has prompted an active search for alternative sources of energy. In addition to solar power, hydrogen is being considered a potential fuel for the future. Hydrogen-run vehicles are being tried. Hydrogen as a fuel has many advantages over the conventional fossil fuels and electric power.

## Hydrides

Binary compounds of the elements (metal or non-metal) with hydrogen are called hydrides. The type of hydride which an element forms depends on its electronegativity and hence the type of bond formed. While there is no sharp division between ionic, covalent and metallic bonding, they are classified as:

- ionic or salt like hydride
- covalent or molecular hydride
- metallic or interstitial hydride

They have been summarised in Fig. 10.4.

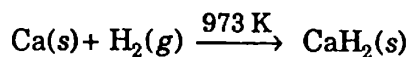
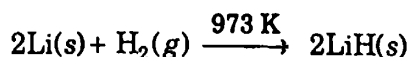
|    |    |                   |   |   |   |   |   |   |    |    |    |    |    |    |    |    |    |
|----|----|-------------------|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|
| 1  | 2  | Transition metals |   |   |   |   |   |   |    |    |    | 13 | 14 | 15 | 16 | 17 | 18 |
| H  | He |                   |   |   |   |   |   |   |    |    |    | B  | C  | N  | O  | F  |    |
| Li | Be |                   |   |   |   |   |   |   |    |    |    | Al | Si | P  | S  | Cl |    |
| Na | Mg | 3                 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |    |    |    |    |    |    |
| K  | Ca |                   |   |   |   |   |   |   |    |    |    | Ga | Ge | As | Se | Br |    |
| Rb | Sr |                   |   |   |   |   |   |   |    |    |    | In | Sn | Sb | Te | I  |    |
| Cs |    | La                |   |   |   |   |   |   |    |    |    | Ti | Pb | Bi | Po | At |    |
| Fr | Ac |                   |   |   |   |   |   |   |    |    |    |    |    |    |    |    |    |

- ☐ Mainly ionic with fixed formula     ☒ Often of uncertain formula; absorbed into metal lattice (Intermediate)  
☐ Covalent, molecular structures

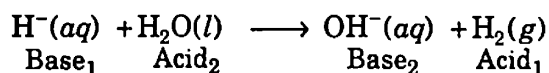
Fig. 10.4 Hydrides of the Elements

## Ionic Hydrides

- They are formed when molecular hydrogen combines directly with any alkali metal or with the alkaline earth metals Ca, Sr or Ba (electropositive metal).

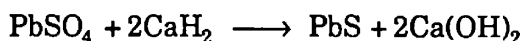
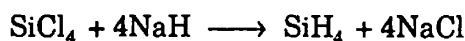
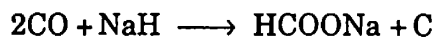


All ionic hydrides are solids that have the high melting point characteristic of ionic compounds and conduct electricity in fused state liberating  $\text{H}_2$  at the anode. Anion of these hydrides is  $\text{H}^-$  which is a very strong **Bronsted** base ( $\text{H}^+$  ion acceptor) and accepts proton from a proton donor such as water:

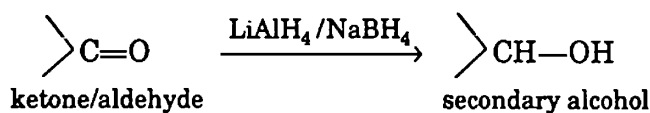
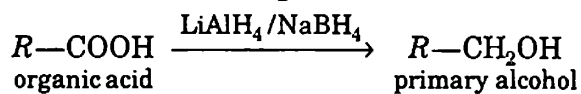


Due to their high reactivity with water, ionic hydrides are used to remove traces of water from organic solvents.

They are powerful reducing agent specially at higher temperature, *e.g.*,



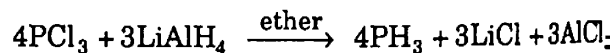
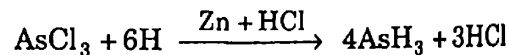
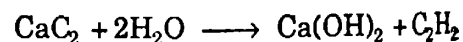
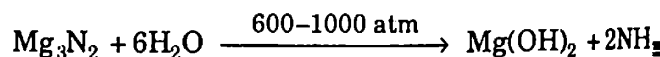
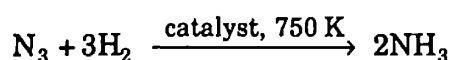
$\text{Li}^+\text{H}^-$  and  $\text{Na}^+\text{H}^-$  are used in making valuable reducing agents like lithium aluminium hydride ( $\text{LiAlH}_4$ ) and sodium borohydride ( $\text{NaBH}_4$ ). These complex hydrides are frequently used in the reduction of aldehydes, ketones, acids and their derivatives of give alcohols.



## Covalent Hydride

Covalent hydrides are formed by elements of comparatively higher electronegativity, generally *p*-block elements and Be and Mg. The bonds in this class of hydrides are mostly covalent in character but in some cases, for example, in HF, the bond may be partially ionic.

The covalent hydrides can be prepared either by direct reaction of non-metals with hydrogen under suitable conditions or by the reaction of  $\text{H}_2\text{O}$  or acids on nitrides, carbides, borides, silicides, stannides of alkali and alkaline earth metals or by the reduction of halides. These are illustrated by the following reactions :



## DEEP Focus

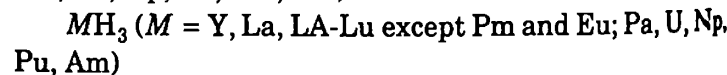
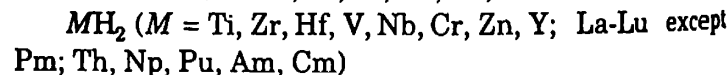
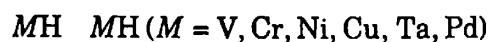
These hydrides have a molecular lattice made up of individual saturated covalent molecules, with only weak van der Waals' forces and in some cases hydrogen bonds holding the molecules together. This accounts for their softness, low melting and boiling points, their volatility and lack of conductivity. Some covalent hydrides are unstable in the presence of air, *e.g.*, stannane,  $\text{SnH}_4$ .

Some covalent hydrides of Groups 2 and 13 are electron deficient. These have structures between ionic and covalent hydrides. These are either dimeric, *e.g.*, boron hydride ( $\text{B}_2\text{H}_6$ ), or polymeric, *e.g.*, beryllium hydride ( $\text{BeH}_2$ )<sub>n</sub>, magnesium hydride ( $\text{MgH}_2$ )<sub>n</sub> and aluminium hydride ( $\text{AlH}_3$ )<sub>n</sub>.

## Metallic Hydrides

On heating, hydrogen reacts with many transition metals, lanthanides and actinides to form metallic hydrides. Most of these have metallic appearance and are less dense than the parent metal. They all conduct heat and electricity though not as well as the parent metal (of ionic hydrides). Unlike the saline hydrides, they are almost always non-stoichiometric, being deficient in hydrogen. For example,  $\text{TiH}_{1.5-1.8}$ ,  $\text{VH}_{0.56}$ ,  $\text{CH}_{1.7}$ ,  $\text{NiH}_{0.6-0.7}$ ,  $\text{PdH}_{0.6-0.8}$ ,  $\text{TaH}_{2.76}$ ,  $\text{LaH}_{2.87}$ ,  $\text{YbH}_{2.55}$ , etc., approach the stoichiometric formulae given in following Table. Most of these hydrides are stable to water up to 375 K but are quantitatively decomposed by acids and show reducing properties.

### Stoichiometric Formulae of Some Metallic Hydrides

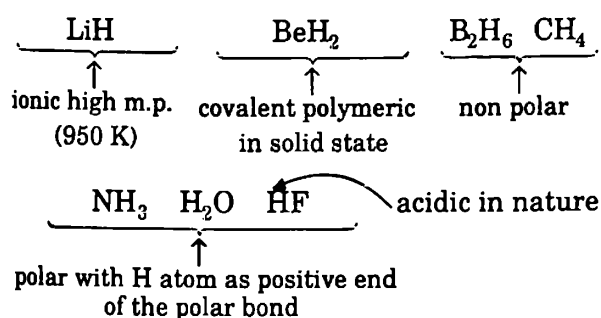


Formerly, these hydrides were termed as interstitial compounds in which hydrogen was thought to be accommodated in the interstices in the metal lattice producing distortion but no change in its type. But recent studies have shown that except for the hydrides of nickel, palladium, cerium and actinium, other hydrides of this class have lattice of a type different from that of the parent metal.

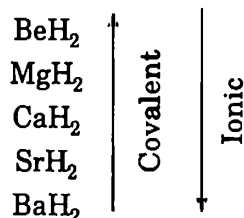
### DEEP Focus

For example, the hexagonal close packed lattice of some lanthanides is transformed to a face-centred cubic lattice in their dihydrides. These interstitial hydrides are poorer conductors of electricity, exhibit less paramagnetism and are more brittle than the parent metal. These characteristics suggest that hydrogen is present in the metal lattice as hydrogen atoms rather than as hydrogen molecules. The single electron of hydrogen is paired with an electron of the metal, thereby reducing the extent of metallic bonding. Breaking of the H—H bond is in agreement with the fact that these metals catalyse reactions of hydrogen.

The physical and chemical properties of these compounds change from ionic to covalent across a given period (moving left to right).



- As we move down any group, the compounds change from covalent to ionic.



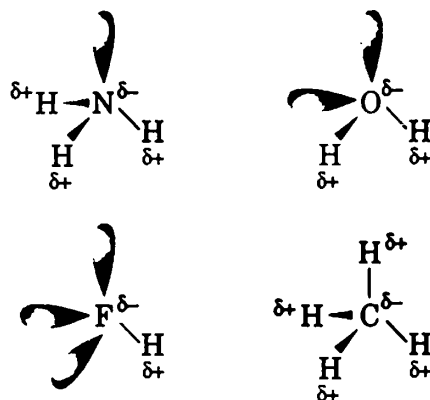
The  $\Delta H_f^\circ$  values (Table 10.4) show that the energetic stability of the covalent hydrides tends to increase on passing from left to right across a period, but to decrease on passing down any group. The main reason for this is the change in the strength of the X—H bond as shown by the bond enthalpy figures in Table 10.4. The attraction of an atom for a shared pair of electrons increases across a

period as nuclear charge increases and atomic radius falls, but decreases down a group as both atomic size and the number of inner screening electrons increase.

Although all of the hydrides shown in Table 10.4 are described as covalent, the bonds are polar to some extent. The degree of this polarity depends upon the electronegativity difference between the two elements concerned. In the case of the Group 14 hydrides, however, this bond polarity does not result in a polar molecule. In the tetrahedral  $\text{XH}_4$  molecule, there is no overall dipole moment as the centre of the  $\delta^+$  charges coincides with the centre of the  $\delta^-$  charge, for example in methane.

As they have no overall dipole, the only forces of attraction between  $\text{XH}_4$  molecules are relatively weak van der Waals' forces due to temporary dipoles. Since, these forces result from mutual repulsion of the electron clouds of neighbouring molecules, they increase as the size of the molecule increases, thus, accounting for the steady increase in the boiling point of the hydrides on passing down group 14.

In the case of the hydrides of Group 15, 16 and 17, bond polarity does result in a permanent molecular dipole.



Permanent dipoles in period 2 hydrides

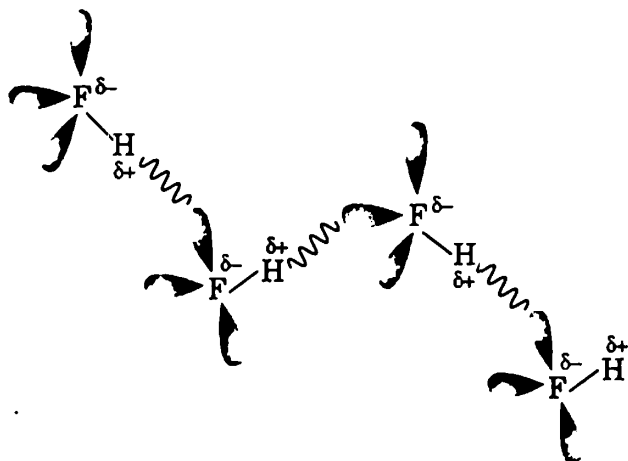
Table 10.4 Some Common Covalent Hydrides of Periods 2-5. Electronegativity Differences in Brackets Indicate that Hydrogen is more Electronegative Than the *p*-Block Element, that is, the Polarity of the Bond is  $X^{\delta+}-H^{\delta-}$

|                                        | Group 14               | Group 15               | Group 16               | Group 17   |
|----------------------------------------|------------------------|------------------------|------------------------|------------|
| <b>Period 2</b>                        | <b>CH<sub>4</sub></b>  | <b>NH<sub>3</sub></b>  | <b>H<sub>2</sub>O</b>  | <b>HF</b>  |
| $\Delta H/\text{kJ mol}^{-1}$          | -74                    | -46                    | -286                   | -271       |
| Bond enthalpy/ $\text{kJ mol}^{-1}$    | +436                   | +431                   | +494                   | +574       |
| Boiling point/K                        | 112                    | 238                    | 373                    | 293        |
| Electronegativity difference (Pauling) | 0.35                   | 0.84                   | 1.24                   | 1.78       |
| <b>Period 3</b>                        | <b>SiH<sub>4</sub></b> | <b>PH<sub>3</sub></b>  | <b>H<sub>2</sub>S</b>  | <b>HCl</b> |
| $\Delta H/\text{kJ mol}^{-1}$          | 34                     | -10                    | +20                    | -92        |
| Bond enthalpy/ $\text{kJ mol}^{-1}$    | +323                   | +323                   | +364                   | +432       |
| Boiling point/K                        | 161                    | 185                    | 213                    | 188        |
| Electronegativity difference (Pauling) | (0.3)                  | (0.01)                 | 0.38                   | 0.96       |
| <b>Period 4</b>                        | <b>GeH<sub>4</sub></b> | <b>AsH<sub>3</sub></b> | <b>H<sub>2</sub>Se</b> | <b>HBr</b> |
| $\Delta H/\text{kJ mol}^{-1}$          | +91                    | +66                    | +73                    | -36        |
| Bond enthalpy/ $\text{kJ mol}^{-1}$    | 289                    | —                      | —                      | +363       |
| Boiling point/K                        | 185                    | 211                    | 232                    | 206        |
| Electronegativity difference (Pauling) | (0.19)                 | (0.02)                 | 0.35                   | 0.76       |
| <b>Period 5</b>                        | <b>SnH<sub>4</sub></b> | <b>SbH<sub>3</sub></b> | <b>H<sub>2</sub>Te</b> | <b>HI</b>  |
| $\Delta H/\text{kJ mol}^{-1}$          | +163                   | +145                   | +100                   | +26        |
| Bond enthalpy/ $\text{kJ mol}^{-1}$    | 253                    | —                      | —                      | +295       |
| Boiling point/K                        | 221                    | 256                    | 269                    | 238        |
| Electronegativity difference (Pauling) | (0.24)                 | (0.2)                  | (0.1)                  | 0.46       |

In these cases, as well as attraction due to temporary dipoles, there is an extra attraction due to these permanent molecular dipoles. The positively charged hydrogen atom will attract a lone pair of electrons on the *p*-block atom of a neighbouring molecule.

### DEEP Focus

As a result of this extra permanent dipole attraction, in any period the boiling points of the Group 15, 16 and 17 hydrides are all higher than that of the non-polar Group 14 hydride. This effect is much greater in period 2 than in the lower periods (Fig. 10.5). Since, the attraction resulting from the presence of N—H, O—H or F—H bonds is much stronger than other permanent dipoles, in these cases only the effect is referred to as *hydrogen bonding*. Typically such 'hydrogen bonds' 5-10% of the strength of a covalent and in the case of water this is enough to make it liquid at room temperature.



Hydrogen bonding in hydrogen fluoride

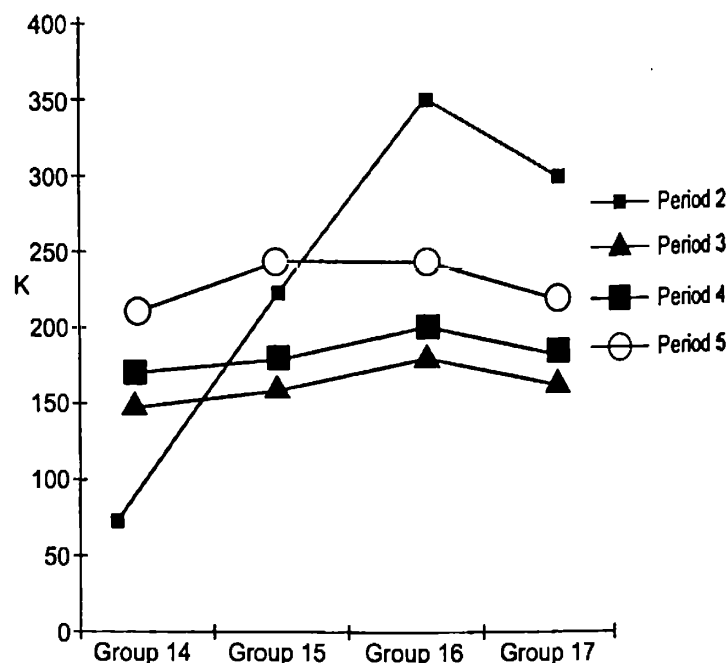
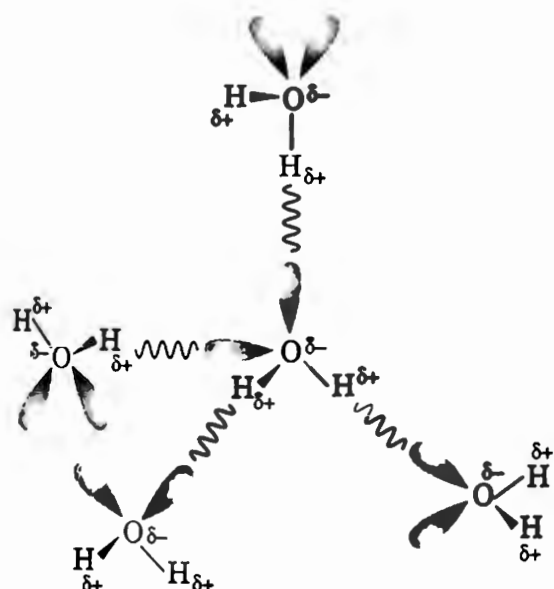


Fig. 10.5 Boiling point of covalent hydrides plotted by period

At first glance it might seem surprising that hydrogen fluoride has a lower boiling point than water, even though it contains the more polar H—F bond. Whilst the individual hydrogen bonds in HF are indeed stronger than those in water, the latter can form more hydrogen bonds. Each water molecule contains two  $H^{\delta+}$  atoms and each  $O^{\delta-}$  has two lone pairs and so may form up to four hydrogen bonds with its neighbours.

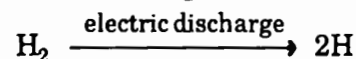


Water can hydrogen bond to several other water molecules.

On average both HF and NH<sub>3</sub> can form two hydrogen bonds with neighbouring molecules and, as expected, hydrogen bonding between the less polar NH<sub>3</sub> molecules results in a lower boiling point for ammonia than hydrogen fluoride.

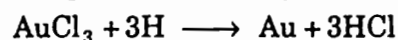
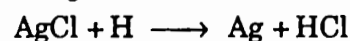
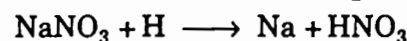
## Atomic Hydrogen

Hydrogen gas dissociates into atoms when it (H<sub>2</sub>) is subjected to an electric discharge under low pressure.

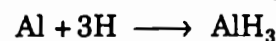
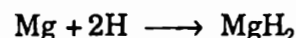
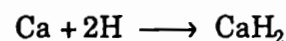
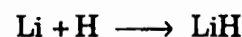


- Atomic hydrogen is very reactive and can be used as a **reducing agent** as well as **oxidising agent**

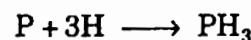
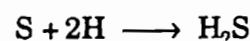
- As a **reducing agent**



- As an **oxidising agent** (when hydrides are formed)



- Reaction with non-metals



## Target Practice 1

- Why does hydrogen resemble the alkali metals?  
.....
- Chemical properties of isotopes of hydrogen are similar. Explain.  
.....
- Select True/False
  - Ortho* and *para* hydrogen forms are different due to difference in their nuclear spins.
  - Ortho* and *para* hydrogen forms are different due to difference in their electron spins.
  - Physical properties of *ortho* and *para* hydrogen are similar.

- Para* hydrogen is more stable at lower temperatures.
- At 100 K, percentage of *ortho* hydrogen in the mixture is 70%.

- Complete the following chemical reactions which take place during the formation of hydrogen
  - $\text{C} + \text{H}_2\text{O} \longrightarrow \dots + \dots$
  - $\text{CH}_4 + \text{H}_2\text{O} \longrightarrow \dots + \dots$
  - $\text{CO} + \text{H}_2\text{O} \longrightarrow \dots + \dots$
  - $\text{CaH}_2 + \text{H}_2\text{O} \longrightarrow \dots + \dots$
- Hydroformylation reaction is the industrial preparation of methanol. Write this reaction .....  $\longrightarrow \text{CH}_3\text{OH}$ .

## Answers

- Hydrogen resembles alkali metals because like alkali metals it also has one electron in s-orbital  
 $\text{H} : 1s^2$   
 $\text{Li} : 1s^2 2s^1$   
 $\text{Na} : [\text{Ne}] 3s^1$
- Most of the chemical properties are governed by the electronic configuration of the element. As the isotopes of hydrogen have the same electronic configuration, their chemical properties are closely similar.

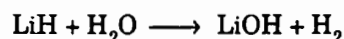
- (i) T (ii) F (iii) F (iv) T (v) F
- $\longrightarrow \text{CO} + \text{H}_2$
  - $\longrightarrow \text{CO} + 3\text{H}_2$
  - $\longrightarrow \text{CO}_2 + \text{H}_2$
  - $\longrightarrow \text{Ca(OH)}_2 + \text{H}_2$
- $\text{CO} + 2\text{H}_2 \longrightarrow \text{CH}_3\text{OH}$

## Practice Exercise 1

1. What is the equation for the nuclear reaction that takes place when tritium undergoes beta decay? What is the product in the reaction?
2. Before natural gas can be used to make hydrogen, it has to be purified. Especially sulphur compounds must not be allowed through; why?
3. If Zn pieces are added into aqueous  $\text{FeCl}_3$  solution, deep yellow colour of  $\text{FeCl}_3$  fades and changes to light green. But

if  $\text{H}_2$  gas is passed into  $\text{FeCl}_3$  solution, there is no change. Explain.

4. For  $\text{H}_2\text{O}$ ,  $K_w = 1 \times 10^{-14}$ ;  $\text{D}_2\text{O}$ ,  $K_w = 3.0 \times 10^{-15}$ . Compare  $[\text{H}^+]$  and  $[\text{D}^+]$  in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . If both are electrolysed, which is liberated faster,  $\text{H}_2$  or  $\text{D}_2$ ?
5. Ionic hydrides are the **ready-made** source of hydrogen. Explain.
6. What is the nature of hydride in the following reaction,

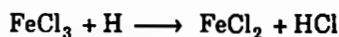


## Answers

1.  ${}^3_1\text{H} \longrightarrow {}^3_2\text{He} + {}^0_{-1}\text{e}$
2. Sulphur is very effective poison of catalysts, so it has to be removed before it reaches the nickel.
3.  $\text{FeCl}_3$  solution is acidic in nature due to hydrolysis:

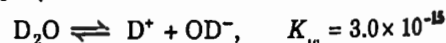


On adding Zn, nascent hydrogen is formed in situ, that being very reactive causes reduction of  $\text{Fe}^{3+}$  (deep yellow) to  $\text{Fe}^{2+}$  (light green). Molecular  $\text{H}_2$  is not effective in this case:



4.  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ ,  $K_w = 1 \times 10^{-14}$

$$\therefore [\text{H}^+] = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7} \text{ M}$$



$$[\text{D}^+] = \sqrt{3.0 \times 10^{-15}} \text{ M}$$

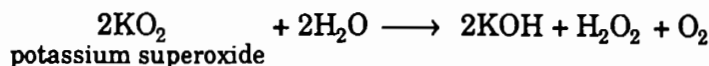
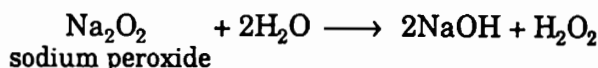
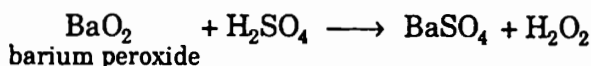
Thus,  $[\text{H}^+] > [\text{D}^+]$

$\text{H}_2$  gas is liberated much faster than  $\text{D}_2$  at cathode.

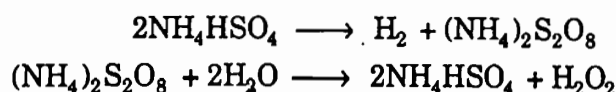
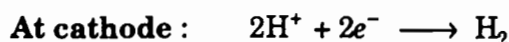
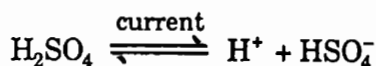
5.  $\text{CaH}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Ca}(\text{OH})_2 + 2\text{H}_2$
6.  $\text{LiH}$  ( $\text{H}^-$ ) is  $\text{H}^+$  acceptor from  $\text{H}_2\text{O}$  and changes to  $\text{H}_2$ . Hence,  $\text{LiH}$  is a Lowry-Bronsted base

## Hydrogen Peroxide

- It is the hydride of oxygen.
- $\text{BaO}_2$  is decomposed by  $\text{H}_2\text{SO}_4$ ;  $\text{Na}_2\text{O}_2$  and  $\text{KO}_2$  by  $\text{H}_2\text{O}$  forming  $\text{H}_2\text{O}_2$ :



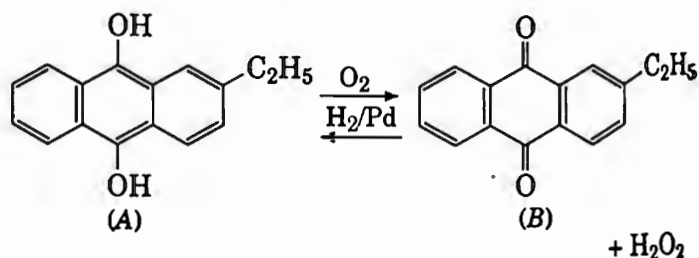
- Electrolysis of  $\text{H}_2\text{SO}_4$  or  $\text{NH}_4\text{HSO}_4$  at high current density using platinum electrodes forms peroxosulphuric acid which on subsequent hydrolysis gives  $\text{H}_2\text{O}_2$ :



This solution is concentrated to 98 per cent by low pressure fractionation.

- Industrially it is obtained by a **Cyclic Process**. 2-ethyl anthraquinol (A) is oxidised by air to 2-ethyl anthraquinone (B) and  $\text{H}_2\text{O}_2$ : (B) is reduced back to (A) with  $\text{H}_2$  at a moderate temperature using Pt, Pd or Raney Ni as a catalyst. The cycle is repeated. The reaction is carried out in a mixture of organic solvents which must:

- dissolve both (A) and (B)

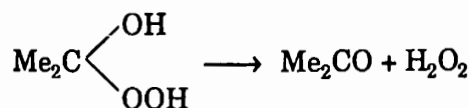
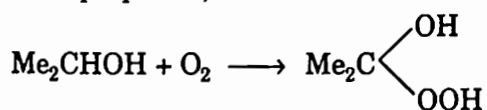


- resist oxidation
- be immiscible with water.

Solvent is generally a mixture of ester and hydrocarbon or octanol and methyl naphthalene.

$\text{H}_2\text{O}_2$  is extracted with water as a 1% solution. This is concentrated under reduced pressure.  $\text{H}_2\text{O}_2$  solutions are stored in plastic or wax coated glass vessels, often with negative catalysts such as urea or sodium stannate added as stabilisers.

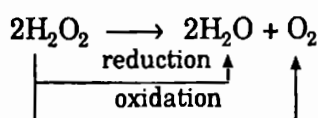
- An alternative process is based on the partial oxidation of 2-propanol ;



- Pure  $\text{H}_2\text{O}_2$  is a colourless liquid which resembles water quite closely. It is more hydrogen bonded than is water so has a higher boiling point and is more dense than  $\text{H}_2\text{O}$ .

| Property      | $\text{H}_2\text{O}_2$ | $\text{H}_2\text{O}$   |
|---------------|------------------------|------------------------|
| boiling point | 152°C (decomposes)     | 100°C                  |
| melting point | -0.4°C                 | 0°C                    |
| density       | 1.4 g cm <sup>-3</sup> | 1.0 g cm <sup>-3</sup> |

- At 68 mmHg pressure, it boils at 84°C.
- $\text{H}_2\text{O}_2$  is unstable and the rate at which it disproportionates, depends on the temperature and concentration. Many impurities catalyse the decomposition, which may become very violent, especially with concentrated solutions.



Catalysts include metal ions  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , metal surfaces such as Pt or Ag,  $\text{MnO}_2$ , charcoal or alkali. They are best stored in polythene bottles in a refrigerator. Traces of complexing agents (e.g., 8-hydroquinoline) or adsorbing material (e.g., sodium stannate) are often added as stabilisers.

- Mixtures of hydrogen peroxides and organic or other easily oxidised materials are dangerously explosive. **Mixture of hydrogen peroxide and hydrazine has been used for rocket propulsion.**

- The ionisation constant of hydrogen peroxide in aqueous solution at 20°C for the acid equilibrium is

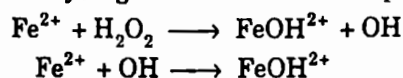
$$\text{H}_2\text{O}_2 \rightleftharpoons \text{H}^+ + \text{HO}_2^-$$

$$K_a = \frac{[\text{H}^+][\text{HO}_2^-]}{[\text{H}_2\text{O}_2]} = 2 \times 10^{-12}$$

In alkaline medium, therefore, it is present as the  $\text{HO}_2^-$  ion.

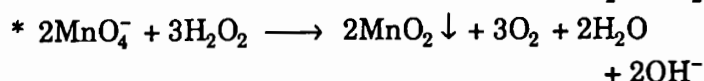
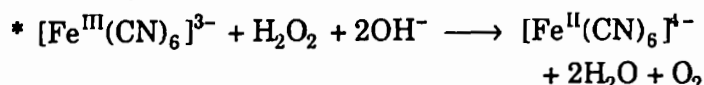
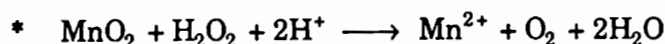
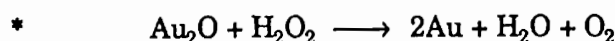
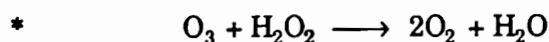
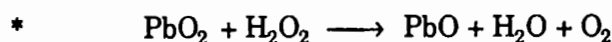
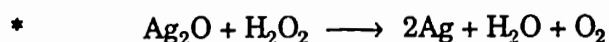
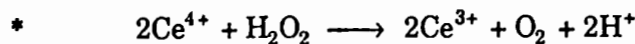
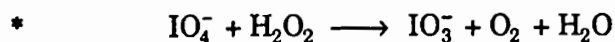
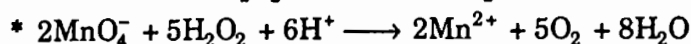
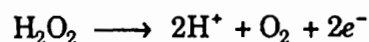
### DEEP Focus

- Many reactions of  $\text{H}_2\text{O}_2$  are radical reactions. The oxidation of  $\text{Fe(II)}$  at low hydrogen ion concentrations proceeds as:



and a mixture of  $\text{H}_2\text{O}_2$  and  $\text{Fe(II)}$  is thus a source of hydroxyl radicals for organic reactions.

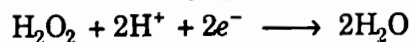
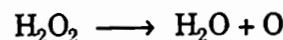
- $\text{H}_2\text{O}_2$  as reducing agent :** (when itself oxidised to  $\text{O}_2$ )



### DEEP Focus

Traces studies using  $^{18}\text{O}$  show that in reactions all the oxygen that is formed comes from the  $\text{H}_2\text{O}_2$ , none from the solvent  $\text{H}_2\text{O}$ , so the O—O bond is not broken.

- $\text{H}_2\text{O}_2$  as an oxidising agent :** (when itself reduced to  $\text{H}_2\text{O}$ )

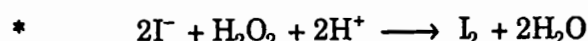
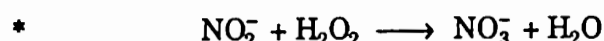
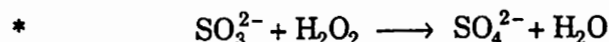
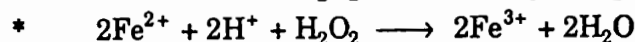
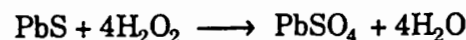


$$\text{and at } [\text{H}^+] = 1 \text{ M, } E^\circ = +1.77 \text{ V}$$

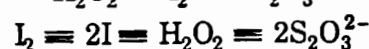
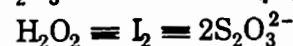
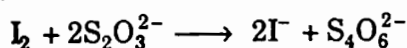
hence, it is a strong oxidising agent.

- Its bleaching action is also due to its oxidising property.

Oil paintings contain  $\text{Pb}^{2+}$  salts which are blackened by atmospheric  $\text{H}_2\text{S}$  (due to  $\text{PbS}$ ).  $\text{PbS}$  (black), on reaction with  $\text{H}_2\text{O}_2$ , changes to  $\text{PbSO}_4$  (white), hence  $\text{H}_2\text{O}_2$  is used to clean oil paintings :



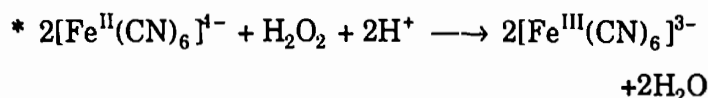
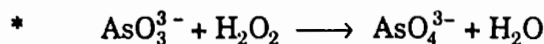
This reaction can be used to estimate  $\text{H}_2\text{O}_2$  iodometrically.  $\text{I}_2$  formed is titrated against  $\text{Na}_2\text{S}_2\text{O}_3$  solution :



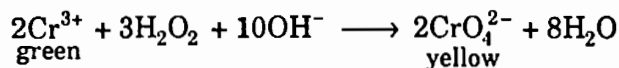
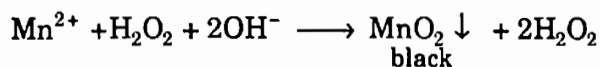
$$\therefore \text{Eq. wt. } (\text{H}_2\text{O}_2) = \left( \frac{\text{mol. wt.}}{2} \right)$$

$$\text{Eq. wt. } (\text{S}_2\text{O}_3^{2-}) = \text{mol. wt.}$$



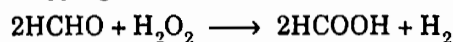


\*  $\text{Mn}^{2+}$  (colourless when dilute) changes to  $\text{MnO}_2$  (black) and  $\text{Cr}^{3+}$  (green) changes to  $\text{CrO}_4^{2-}$  (yellow) in alkaline  $\text{H}_2\text{O}_2$ .



### DEEP Focus

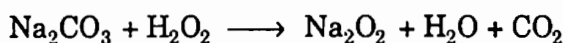
- HCHO (formaldehyde) is oxidised to HCOOH (formic acid) in presence of pyrogallol and is itself reduced to hydrogen.



The reaction in the dark is accompanied by emission of light (chemiluminescence).

- As an acid :**

$\text{H}_2\text{O}_2$  decomposes  $\text{CO}_2$  from carbonates and thus behaves as an acid. It turns blue litmus red but aqueous solutions has no effect.

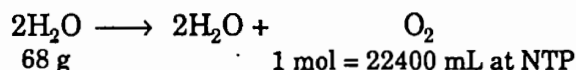


A 30% solution of  $\text{H}_2\text{O}_2$  is sold in the market under the trade name **perhydrol**. This is also known as “100 volume” peroxide.

- Concentration Determination :**

Concentration of  $\text{H}_2\text{O}_2$  is expressed in terms of “volume of  $\text{O}_2$ ”

“10 volume”  $\text{H}_2\text{O}_2$  means that 1 mL of  $\text{H}_2\text{O}_2$  at NTP gives 10 mL  $\text{O}_2$  gas. These values can be changed into other concentration terms like density,  $\text{g L}^{-1}$ , normality and molarity.



$$? \quad \quad \quad x \text{ mL}$$

$$22400 \text{ mL O}_2 \text{ is from} = 68 \text{ g H}_2\text{O}_2 \text{ at NTP}$$

$$x \text{ mL O}_2 \text{ gas is from} = \frac{68x}{22400} \text{ g H}_2\text{O}_2 \text{ NTP}$$

This amount is in 1 mL  $\text{H}_2\text{O}_2$  (by definition)

$$\text{Thus,} \quad 1 \text{ mL H}_2\text{O}_2 = \frac{68x}{22400} \text{ g}$$

$$\therefore \quad \text{density} = \frac{68x}{22400} \text{ g/mL}$$

$$\text{conc. in g/L} = \frac{68x}{22400} \times 1000$$

$$\text{g/L conc.} = \frac{680x}{224} \text{ g/L}$$

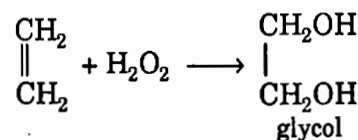
$$\% \text{ conc.} = \frac{68x}{224}$$

$$\text{Normality (N)} = \frac{\text{conc in g/L}}{\text{equiv. wt.}} = \frac{680x}{224} \times \frac{1}{17}$$

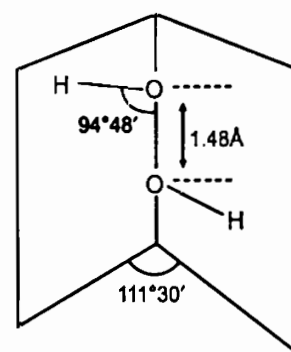
$$N = \frac{x}{5.6}$$

$$\text{Molarity (M)} = \frac{\text{conc. in g/L}}{\text{mol. wt.}} = \frac{680x}{224} \times \frac{1}{34}$$

$$M = \frac{x}{11.2}$$

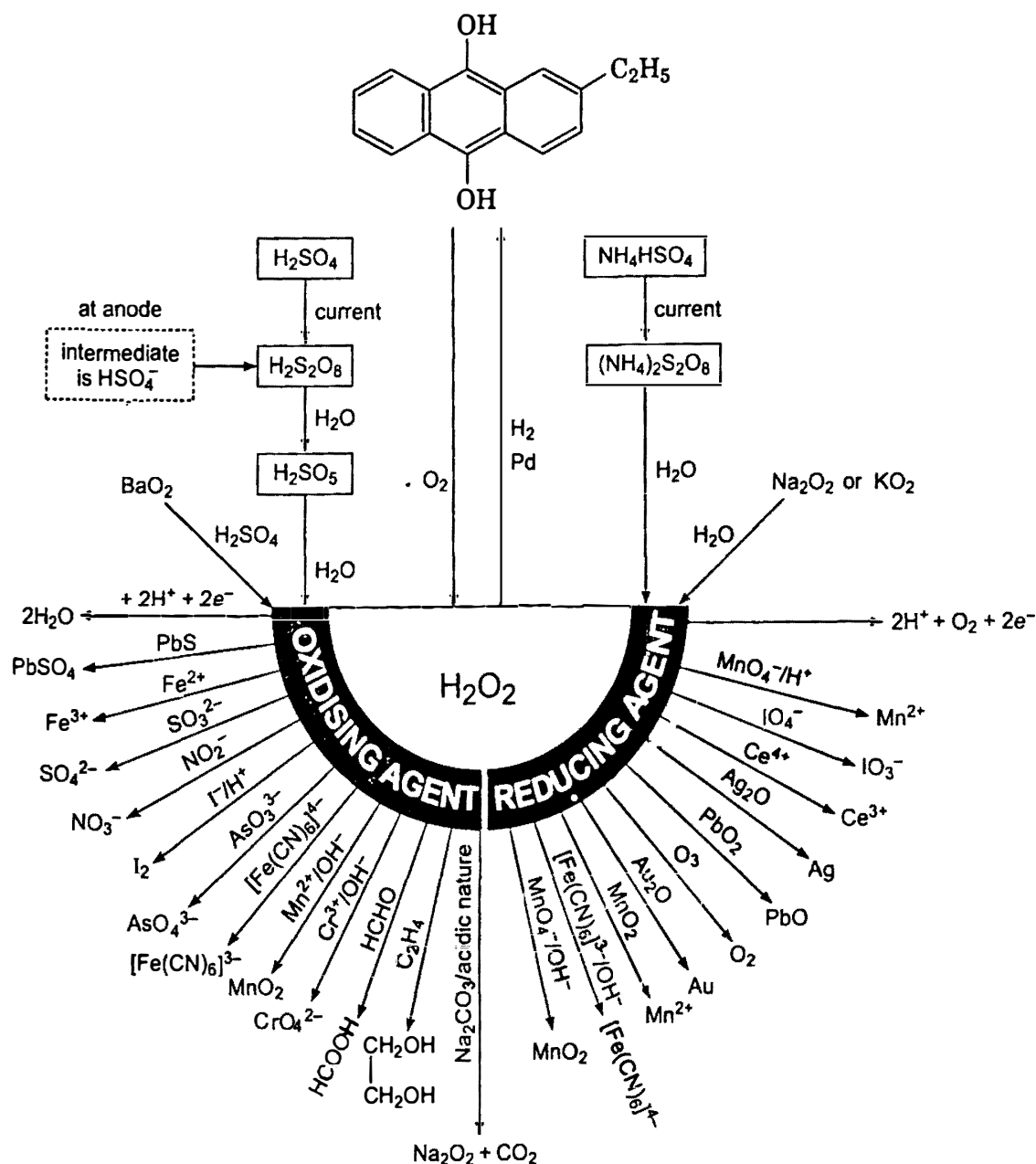


This reaction confirms the presence of two  $-\text{OH}$  groups in  $\text{H}_2\text{O}_2$



- $\text{H}_2\text{O}_2$  finds use

- as a bleaching agent
- as an antiseptic in surgery.
- as a fuel for rockets (85–90% solution).



## Target Practice 2

- Write ionic reactions showing  $\text{H}_2\text{O}_2$  as
  - Reducing agent : .....
  - Oxidising agent : .....
- $\text{H}_2\text{O}_2$  is used to clean oil-paintings. Write reactions making paintings black and then cleaning with  $\text{H}_2\text{O}_2$ .  
.....  
.....
- Specify the meaning of "10 volume"  $\text{H}_2\text{O}_2$ .  
.....  
.....
- Molarity of  $\text{H}_2\text{O}_2$  solution is  $0.01 \text{ mol L}^{-1}$ . Thus, its "volume" concentration is .....

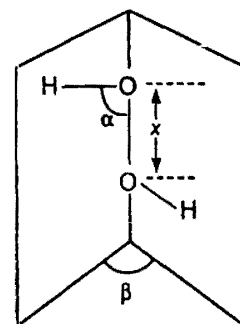
- $\text{H}_2\text{O}_2$  behaves as an acid. Write reaction  
.....  
.....

- Structure of  $\text{H}_2\text{O}_2$  is represented as

Angle  $\angle \alpha = \dots\dots\dots$

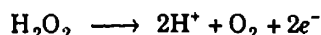
Angle  $\angle \beta = \dots\dots\dots$

Bond-angle length  $x = \dots\dots\dots$

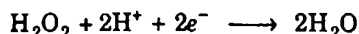


## Answers

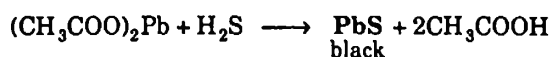
1. (a) Reducing agents :



- (b) Oxidising agents :

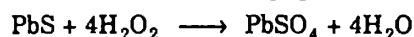


2. Oil paints contain lead acetate (white) which is blackened by atmospheric
- $\text{H}_2\text{S}$
- due to formation of
- $\text{PbS}$
- (black).

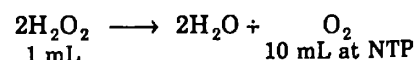


$\text{H}_2\text{O}_2$  oxidises  $\text{PbS}$  (black) to  $\text{PbSO}_4$  (white)

Thus, oil-paintings are cleaned by  $\text{H}_2\text{O}_2$



3. It means that 1 mL
- $\text{H}_2\text{O}_2$
- on decomposition gives 10 mL of
- $\text{O}_2$
- gas at NTP



$$4. \text{ Molarity} = \frac{x \text{ volume}}{11.2}$$

$$\therefore \text{ Volume concentration} = 11.2 \times 0.01$$

$$= \text{"0.112" volume}$$



$$6. \angle\alpha = 94^\circ 48'$$

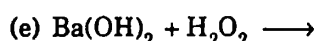
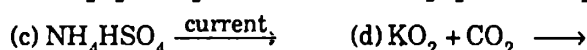
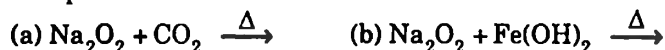
$$\angle\beta = 111^\circ 30'$$

$$x = 1.48 \text{ \AA}$$

## Practice Exercise 2

- 1.
- $\text{H}_2\text{O}_2$
- is used to counteract
- $\text{Cl}_2$
- . How does it act in this process?

2. Complete :



3. When
- $\text{H}_2\text{O}_2$
- reacts with
- $\text{O}_3$
- , is there any change in magnetic behaviour of
- $\text{O}_3$
- ?

4. Represent the following by chemical equations :

(a) Alkaline  $\text{Cr}^{3+}$  salts are oxidised by  $\text{H}_2\text{O}_2$ .

(b)  $\text{H}_2\text{O}_2$  is added to a mixture of conc.  $\text{H}_2\text{SO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ .

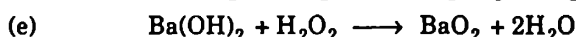
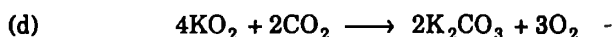
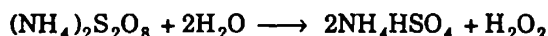
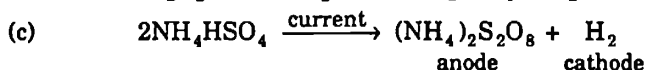
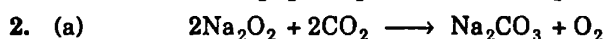
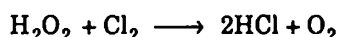
5. What do you conclude about
- $\text{H}_2\text{O}_2$
- from the reaction



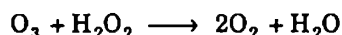
6. When a few drops of blood are added to aqueous
- $\text{H}_2\text{O}_2$
- , it (
- $\text{H}_2\text{O}_2$
- ) decomposes rapidly. Explain.

## Answers

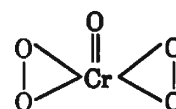
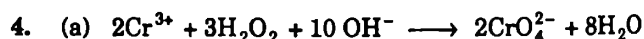
- 1.
- $\text{H}_2\text{O}_2$
- acts as a reducing agent to counteract
- $\text{Cl}_2$



3. Peroxide (
- $\text{O}_2^{2-}$
- ) is diamagnetic and
- $\text{O}_3$
- is also diamagnetic. When both react
- $\text{O}_2$
- and
- $\text{H}_2\text{O}$
- are formed:

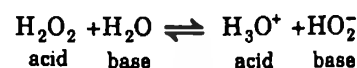


$\text{O}_2$  is paramagnetic. Thus,  $\text{O}_3$  (diamagnetic) is oxidised to  $\text{O}_2$  (paramagnetic) but  $\text{H}_2\text{O}_2$  (diamagnetic) has no effect in its property as  $\text{H}_2\text{O}$  is also diamagnetic.



( $\text{CrO}_5$  gives blue colour in ethereal layer; it is diperoxide)

5. This indicates that
- $\text{H}_2\text{O}_2$
- behaves as acid (though weak)

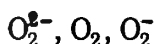


6. The decomposition of
- $\text{H}_2\text{O}_2$
- is catalysed by
- catalase**
- , an enzyme present in blood. There is formation of bubbles due to
- $\text{O}_2$
- .

# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** Compare bond lengths, bond order and magnetic behaviour of



**Solution** Based on molecular orbital theory :

$$\text{bond order of } \text{O}_2^{2-} = 1$$

$$\text{O}_2^- = 1.5$$

$$\text{O}_2 = 2.0$$

Greater the bond order, smaller the bond length, thus bond length of  $\text{O}_2 < \text{O}_2^- < \text{O}_2^{2-}$

$\text{O}_2$  has two unpaired electrons hence, paramagnetic,

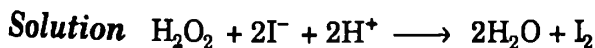
$\text{O}_2^-$  has one unpaired electron hence, paramagnetic,

$\text{O}_2^{2-}$  is without unpaired electron hence diamagnetic.

**Problem 2.** When blood is added to a solution of  $\text{H}_2\text{O}_2$ , the solution bubbles furiously. This reaction is also observed when  $\text{H}_2\text{O}_2$  is poured on a skin wound to cleanse it. What is the overall reaction that occurs?

**Solution** An enzyme or biological catalyst (called catalase), present in tissue and in blood, decomposes the  $\text{H}_2\text{O}_2$  and produces bubbles of  $\text{O}_2$ . The natural function of this enzyme is to prevent the accumulation of  $\text{H}_2\text{O}_2$  in the body, since such a build-up of  $\text{H}_2\text{O}_2$  could damage tissue.

**Problem 3.** To 25 mL  $\text{H}_2\text{O}_2$ , excess of acidified solution of KI was added. The iodine liberated required 20 mL of 0.3 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Calculate volume strength of  $\text{H}_2\text{O}_2$  solution.



$$N_1 V_1 = N_2 V_2$$



$$N_1 \times 25 = 0.3 \times 20$$

$$N_1 = 0.24 \text{ N}$$

Normality of  $\text{H}_2\text{O}_2$  is related to "x volume" strength by relation

$$N = \frac{x}{5.6}$$

$\therefore$

$$x = N_1 \times 5.6$$

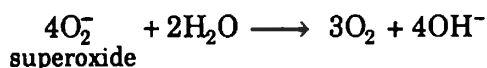
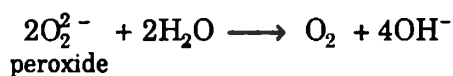
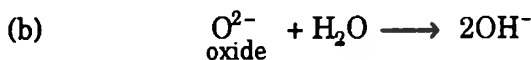
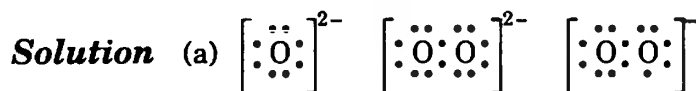
$$= 0.24 \times 5.6$$

$$= \text{"1.344 volume"}$$

**Problem 4.** (a) Give structures of  $\text{O}^{2-}$ ,  $\text{O}_2^{2-}$  and  $\text{O}_2^-$ .

(b) What is their behaviour towards  $\text{H}_2\text{O}$ ?

(c) Give applications of  $\text{H}_2\text{O}_2$  and  $\text{KO}_2$ .

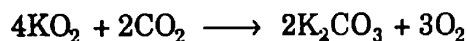


All the three ions are unstable towards  $\text{H}_2\text{O}$  and give alkaline solution. The decomposition of  $\text{O}_2^{2-}$  and  $\text{O}_2^-$  involve oxidation and reduction. Both of these ions, especially  $\text{O}_2^-$ , are good oxidising agents.

(c)  $\text{H}_2\text{O}_2$  is used as :

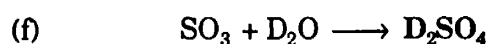
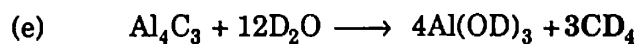
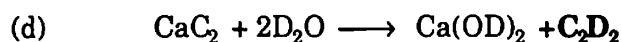
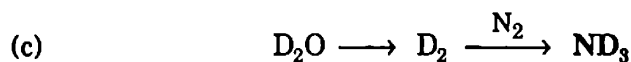
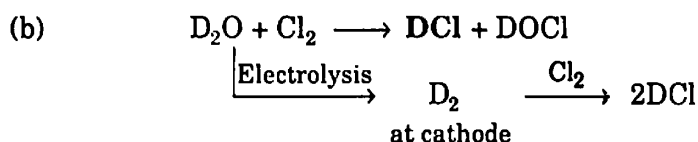
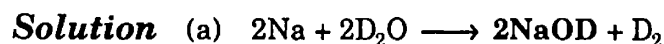
- bleaching agent
- a substitute for  $\text{Cl}_2$  in water and sewage treatment
- an antiseptic in curing wounds.

$\text{KO}_2$  is used in **life supports** in spacecrafts, submarines and emergency breathing apparatus since it absorbs  $\text{CO}_2$  and releases  $\text{O}_2$

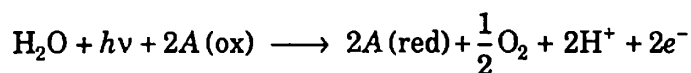


**Problem 5.** Starting with deuterium oxide ( $\text{D}_2\text{O}$ ), describe how you would prepare?

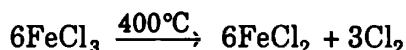
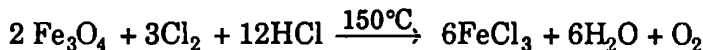
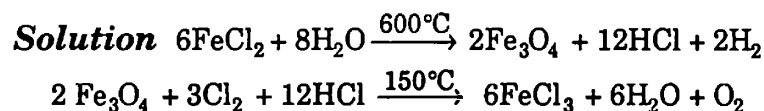
- (a)  $\text{NaOD}$ , (b)  $\text{DCl}$ , (c)  $\text{ND}_3$ , (d)  $\text{C}_2\text{D}_2$ ,  
(e)  $\text{CD}_4$ , (f)  $\text{D}_2\text{SO}_4$



**Problem 6.** A thermochemical cycle for hydrogen production involves at least one element (say Cu) that can exist in two different oxidation states; in a typical cycle A (ox) represents oxidised form and A (red) represents reduced form in a photolytic production of  $\text{H}_2$  as given below:



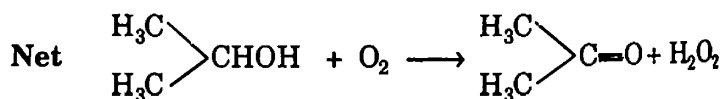
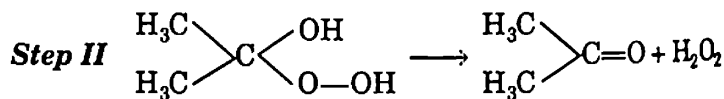
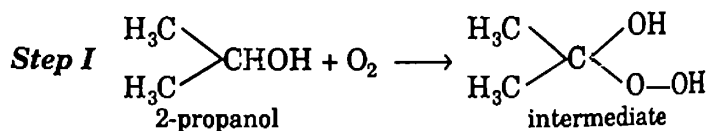
Starting with  $\text{FeCl}_2$ ,  $\text{H}_2\text{O}$  and  $\text{Cl}_2$ , explain formation of  $\text{H}_2$ . You may consider oxidised species as  $\text{FeCl}_3$ .



Various devices may be employed to get round the difficulty created by the simultaneous production of the two gases ( $\text{H}_2$  and  $\text{O}_2$ )

**Problem 7.** Hydrogen peroxide can also be obtained by partial oxidation of 2-propanol. Outline the scheme of this oxidation.

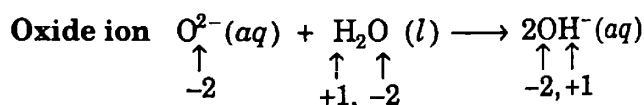
**Solution**



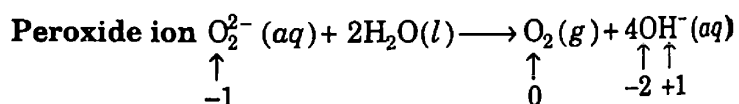
**Problem 8.** Oxygen forms three types of oxides:  $\text{O}^{2-}$ ,  $\text{O}_2^{2-}$  and  $\text{O}_2^-$ . Classify them as base/acid when reacted with  $\text{H}_2\text{O}$ . Also classify the reaction



The ions are all strong **Bronsted-Lowry bases** and react with water as follows:

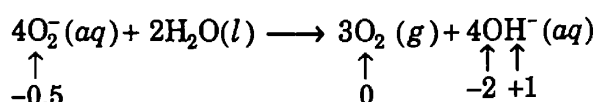


There is no change in oxidation number of O or H, hence, it is simply **hydrolysis** of  $\text{O}^{2-}$ .



There is change in oxidation number of O, thus it is a **redox reaction** (disproportionation of  $\text{O}_2^{2-}$ )

**Superoxide ion**



This is also a redox reaction (disproportionation of  $\text{O}_2^-$ )

# Master Exercises

## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

1. Which of the following compounds would be expected to form intermolecular hydrogen bonds in the liquid state?

- (a)  $\text{CH}_3\text{OCH}_3$                       (b)  $\text{CH}_4$   
(c)  $\text{HF}$                               (d)  $\text{CH}_3\text{CO}_2\text{H}$   
(e)  $\text{Br}$                                 (f)  $\text{CH}_3\text{OH}$

2. What is meant by metallisation of hydrogen?

3. Name the binary compounds of hydrogen.

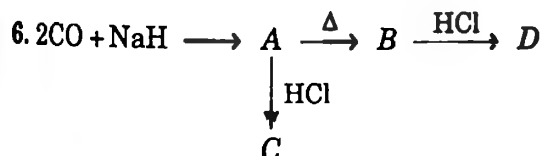
4. Hydrides are reducing agent. Explain

5. (a) Hydrides of boron are called .....

(b) Hydrides of silicon are called .....

(c) Hydrides of carbon are called .....

(d) Hydrides of that can reduce aldehydes to alcohol .....

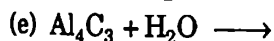
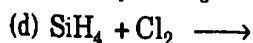
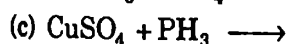
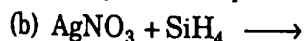


*B* and *D* decolourise  $\text{KMnO}_4$ /acidic

*C* reduces Tollen's reagent

What are *A* to *D*?

7. Complete the following reactions :



8. Name the hydrides used in nuclear reaction technology.

### Analytical Questions

1. A 1 g sample of  $\text{H}_2\text{O}_2$  solution containing *x* per cent  $\text{H}_2\text{O}_2$  by weight required *x* mL of  $\text{KMnO}_4$  for complete oxidation in acidic medium. Calculate normality of  $\text{KMnO}_4$  solution.

2. A 5.0 mL of  $\text{H}_2\text{O}_2$  solution liberates 0.508 g of  $\text{I}_2$  from an acidified KI solution. Calculate the strength of  $\text{H}_2\text{O}_2$  solution in terms of volume strength at STP.

3. You have been given two liquids (*A*) and (*B*) made of same atoms. Both are diamagnetic. Liquid (*A*) +  $\text{KI}/\text{H}^+$  + starch  $\longrightarrow$  blue colour, liquid (*B*) is neutral to litmus and also does not give above test with starch. Identify (*A*) and (*B*).

4.  $\text{Na}[\text{Cr}(\text{OH})_4]$  green solution changes to yellow colour solution when boiled with  $\text{H}_2\text{O}_2$ . Yellow solution changes to orange on acidification. Write reactions of these chemical changes.

5.  $\text{H}_2\text{O}_2$  ionises as:



If pH of  $\text{H}_2\text{O}_2$  at  $20^\circ\text{C}$  is found to be 5.91, calculate ionic product (auto-protolysis constant) of  $\text{H}_2\text{O}_2$ .

6. To prepare  $\text{H}_2$  from water, would you allow water to react with an oxidising agent or a reducing agent? Which of the following metals could be used in the reaction?

(a) Ag

(b) Al

(c) Au

(d) Ca

7. Which of the following molecules have similar properties and which have quite different properties?

(a)  $\text{H}_2^{16}\text{O}$

(b)  $\text{D}_2^{17}\text{O}$

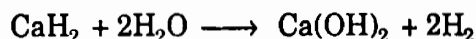
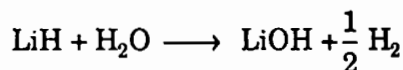
(c)  $\text{H}_2^{16}\text{O}_2$

(d)  $\text{H}_2^{17}\text{O}$

(e)  $\text{D}_2^{17}\text{O}_2$

8. Ionic metal hydrides react with water to give hydrogen gas and an aqueous solution of the metal hydroxide.

- (a) On reaction of equal masses of LiH and CaH<sub>2</sub> with water, which compound gives more H<sub>2</sub>?  
 (b) How many kilograms of CaH<sub>2</sub> is needed to fill a 100 L tank with compressed H<sub>2</sub> gas at 150 atm pressure and at 25°C? (Li = 9, H = 1, Ca = 40)

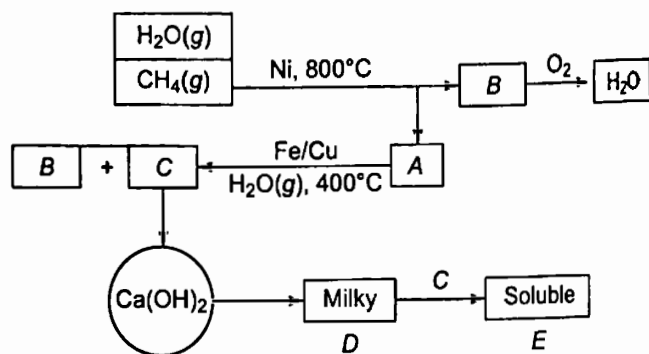


9. Which of the following are oxidised by water? Which are reduced by water? Which undergo a disproportionation reaction when treated with water?

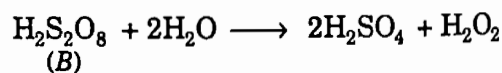
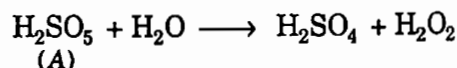
- (a) Cl<sub>2</sub> (b) F<sub>2</sub>  
 (c) K (d) Br<sub>2</sub>

10. How many kilograms of water must be processed to obtain 2.0 L of D<sub>2</sub> at 25°C and 0.90 atm? Assume that deuterium abundance is 0.015 per cent and that recovery is 80 per cent.

11. Identify A to E in the following



12. What conclusion can you draw about the structures of A, and B based on following reactions?



## Exercise 2

### (Stage 2 : High Skill Problem Solving)

#### Only One Option Correct

1. H<sub>2</sub> gas is liberated at cathode and anode both by electrolysis of the following aqueous solution except in

- (a) NaH (b) HCOONa  
 (c) NaCl (d) LiH

2. **Statement S:** Trimethyl ammonium hydroxide (A) is a weaker base than tetramethyl ammonium hydroxide (B).

**Reason R:** O of OH group in (A), is hydrogen bonded to the Me<sub>3</sub>NH—group while in (B), hydrogen bonding can't occur.

- (a) S and R both are correct  
 (b) S is correct but R is incorrect  
 (c) S is incorrect but R is correct  
 (d) S and R both are incorrect

3. In the absence of hydrogen bonding, boiling point of water would have been

- (a) 100°C (b) 0°C  
 (c) -100°C (d) 373°C

4. Which is most volatile out of *o*-, *m*- and *p*-nitrophenol?

- (a) *o*- (b) *m*-  
 (c) *p*- (d) All are equally volatile

5. Which is correct order of boiling point of VA, VIA and VIIA hydride?

- (a) NH<sub>3</sub> > SbH<sub>3</sub> > AsH<sub>3</sub> > PH<sub>3</sub>

- (b) H<sub>2</sub>O > H<sub>2</sub>Te > H<sub>2</sub>Se > H<sub>2</sub>S

- (c) HF > HI > HBr > HCl

- (d) All of the above are correct

6. Which statements is/are correct?

- (a) Boiling point of H<sub>2</sub>O, NH<sub>3</sub>, HF are maximum in their respective group due to intermolecular H-bonding  
 (b) Boiling point of CH<sub>4</sub> out of CH<sub>4</sub>, SiH<sub>4</sub>, GeH<sub>4</sub> and SnH<sub>4</sub> is least due to lack of H-bonding  
 (c) Formic acid forms dimer by H-bonding  
 (d) All the above are correct statements

7. H<sub>2</sub>O<sub>2</sub> can be obtained when following reacts with H<sub>2</sub>SO<sub>4</sub> except with

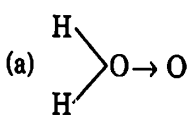
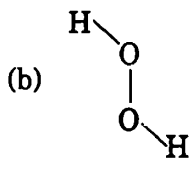
- (a) PbO<sub>2</sub> (b) BaO<sub>2</sub>  
 (c) Na<sub>2</sub>O<sub>2</sub> (d) SrO<sub>2</sub>

8. The set of elements which could form stable, covalent hydrogen bonded hydrides are

- (a) nitrogen, oxygen and fluorine  
 (b) lithium, sodium and potassium  
 (c) sulphur, selenium and tellurium  
 (d) chlorine, bromine and iodine

9. The fuel gas obtained by blowing steam over incandescent coal is known as

- (a) coal gas (b) water gas  
 (c) producer gas (d) natural gas

10. Steam is passed over red hot carbon and the gaseous products cooled and passed first through a solution of alkali, then through ammoniacal cuprous chloride and then through water. What is finally collected?  
 (a)  $\text{CO}_2$   
 (b) A mixture of hydrocarbons  
 (c)  $\text{CO} + \text{H}_2$   
 (d)  $\text{H}_2$
11. Which among the following is a hydride?  
 (a) Rongalite (b) Nitrolim  
 (c) Hydrolith (d) Minium
12. Which of the following easily reacts with water producing hydrogen?  
 (a)  $\text{PH}_3$  (b)  $\text{B}_2\text{H}_6$   
 (c)  $\text{CH}_4$  (d)  $\text{H}_2\text{S}$
13. How does  $\text{H}_2\text{O}_2$  differ from  $\text{O}_3$  in its chemical action?  
 (a) In oxidising  $\text{PbS}$  to  $\text{PbSO}_4$   
 (b) In liberating  $\text{I}_2$  from  $\text{KI}$   
 (c) In decolorising acidified  $\text{KMnO}_4$   
 (d) In oxidising  $\text{K}_4[\text{Fe}(\text{CN})_6]$  to  $\text{K}_3[\text{Fe}(\text{CN})_6]$
14. Which of the following statements about  $\text{H}_2\text{O}_2$  is not true?  
 (a)  $\text{H}_2\text{O}_2$  is used to clean oil paintings  
 (b)  $\text{H}_2\text{O}_2$  acts as oxidising as well as reducing agent  
 (c) Two hydroxyl groups in  $\text{H}_2\text{O}_2$  lie in the same plane  
 (d) It retains same structure in liquid and solid form
15.  $\text{H}_2\text{O}_2$  is used as but not as  
 (a) oxidant, reductant (b) bleaching agent  
 (c) antiseptic (d) catalyst
16. Which is accepted structure of  $\text{H}_2\text{O}_2$  in gas phase?  
 (a)  (b)   
 (c) Both (a) and (b) (d) None of these
17. "10 volume"  $\text{H}_2\text{O}_2$  means  
 (a) 1 mL  $\text{H}_2\text{O}_2$  gives 10 mL  $\text{O}_2$  at NTP  
 (b) 1 g  $\text{H}_2\text{O}_2$  gives 10 mL  $\text{O}_2$  at NTP  
 (c) 1 mol  $\text{H}_2\text{O}_2$  gives 10 mL  $\text{O}_2$  at NTP  
 (d) none of the above is correct
18. Industrially  $\text{H}_2\text{O}_2$  is obtained from  
 (a) 2-ethyl anthraquinol by oxidation and then reduction in a cyclic process  
 (b)  $\text{H}_2\text{SO}_5$   
 (c)  $\text{H}_2\text{S}_2\text{O}_8$   
 (d)  $\text{BaO}_2$
19. Density of  $\text{H}_2\text{O}$  is maximum at  
 (a)  $0^\circ\text{C}$  (b)  $100^\circ\text{C}$   
 (c)  $-273^\circ\text{C}$  (d)  $4^\circ\text{C}$
20. Temporary hardness and permanent hardness in water can be removed respectively by addition of  
 (a)  $\text{CaO}$ ,  $\text{CaCO}_3$  (b)  $\text{CaO}$ ,  $\text{Na}_2\text{CO}_3$   
 (c)  $\text{Na}_2\text{CO}_3$ ,  $\text{CaO}$  (d)  $\text{NaHCO}_3$ ,  $\text{CaCl}_2$
21. Decomposition of  $\text{H}_2\text{O}_2$  can be prevented by addition of  
 (a) ferrous sulphate (b) oxalic acid  
 (c) ozone (d) glycerol
22. Which is true statement?  
 (a) The layer of ice on the surface of river in the winter acts as a thermal insulator between the water below and the air above  
 (b) The fish and other marine organisms are enabled to survive long periods of freezing weather due to the fact that ice is lighter than water  
 (c) Both (a) and (b) are correct  
 (d) None of the above is correct
23. Hydrides of metals are named like  
 (a) alkane (b) alkene  
 (c) alkyne (d) none is correct
24. In water, or in aqueous solutions of  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ , proton exists as  
 (a)  $\text{H}_3\text{O}^+$  (b)  $\text{H}(\text{H}_2\text{O})_4^+$   
 (c)  $\text{H}(\text{H}_2\text{O})_n^+$  (d) all are correct
25. Hydrogen  
 (a) is placed in I A since it forms monovalent cation  $\text{H}^+$   
 (b) is placed in VII A (halogen family) since it forms monovalent anion  $\text{H}^-$   
 (c) is placed in IV A (carbon family) since both have a half filled shell of electrons  
 (d) follows all of the above facts
26. Which is true statement about  $\text{H}_2\text{O}$ ?  
 (a) Hardness can be removed by passing through ion exchange resin  
 (b) Its presence can be detected by anhydrous  $\text{CuSO}_4$   
 (c) It is amphiprotic  
 (d) All the above are correct statement
27.  $\text{H}_2\text{O}_2$  is "5.6 volume", then  
 (a) it is 1.7% weight by volume  
 (b) it is 1 N  
 (c) both (a) and (b) are true  
 (d) none of the above is true
28. Bond angles  $\text{H}-\text{O}-\text{H}$  and  $\text{H}-\text{O}-\text{O}-\text{H}$  in water and hydrogen peroxide respectively are  
 (a)  $104.5^\circ$  in both (b)  $94.8^\circ$  in both  
 (c)  $104.5^\circ$ ,  $94.8^\circ$  (d)  $94.8^\circ$  and  $104.5^\circ$
29.  $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$   
 This represents  
 (a) oxidation of  $\text{H}_2\text{O}_2$   
 (b) reduction of  $\text{H}_2\text{O}_2$   
 (c) disproportionation of  $\text{H}_2\text{O}_2$   
 (d) acidic nature of  $\text{H}_2\text{O}_2$



30. Which is a source of nascent hydrogen?

I :  $\text{Zn} + \text{dil. HCl}$ ,

II :  $\text{CH}_3\text{OH} + \text{Na}$

III : Electrolysis of  $\text{H}_2\text{O}$

IV : Silent electric discharge

(a) I, II

(b) II, III

(c) I, II, III, IV

(d) IV

31. Select correct statement(s) about lime light.

(a) Oxy-hydrogen flame

(b) Used in welding

(c) Temperature of lime light is sufficient to melt even platinum

(d) All the above are correct

32.  $\text{H}_2$  is adsorbed on palladium surface. It is a case of

(a) occlusion

(b) diffusion

(c) effusion

(d) electro-osmosis

33.  $\text{D}_2\text{O}$  (heavy water) and  $\text{H}_2\text{O}$  differ in following except in

(a) freezing point

(b) density

(c) ionic product of water

(d) its reaction with sodium

34. (A)  $\text{FeCl}_3$  solution +  $\text{Zn} \longrightarrow$  product X

(B)  $\text{FeCl}_3$  solution +  $\text{H}_2$  gas  $\longrightarrow$  product Y

$\text{FeCl}_3$  solution gives blue colour with  $\text{K}_4[\text{Fe}(\text{CN})_6]$  hence

(a) X also gives blue colour with  $\text{K}_4[\text{Fe}(\text{CN})_6]$

(b) Y also gives blue colour with  $\text{K}_4[\text{Fe}(\text{CN})_6]$

(c) both X and Y give blue colour with  $\text{K}_4[\text{Fe}(\text{CN})_6]$

(d) none gives colour with  $\text{K}_4[\text{Fe}(\text{CN})_6]$

35.  $\text{H}^+$ ,  $\text{D}^+$  and  $\text{T}^+$  differ in all except in

(a) number of electrons

(b) number of neutrons

(c) ionic mass

(d) all of these

36. Which is radioactive isotope of hydrogen?

(a)  ${}^1_1\text{H}$

(b)  ${}^2_1\text{H}$

(c)  ${}^3_1\text{H}$

(d) All of these

37. Which is true about different forms of hydrogen?

(a) *Ortho* hydrogen has same spins of two nuclei clockwise or anticlockwise

(b) *Para* hydrogen has different spins of two nuclei

(c) At absolute zero, there is 100% *para* form and at high temperature, there is 75% *ortho* form

(d) All the above are correct

38. Which is not correct statement?

(a) *s*-block elements, except Be and Mg, form ionic hydride

(b)  $\text{BeH}_2$ ,  $\text{MgH}_2$ ,  $\text{CuH}_2$ ,  $\text{ZnH}_2$ ,  $\text{CaH}_2$  and  $\text{HgH}_2$  are intermediate hydride

(c) *p*-block elements form covalent hydride

(d) *d*- and *f*-block elements form ionic hydride

39.  $\text{H}_2$  can be obtained from

(a) water gas ( $\text{CO} + \text{H}_2$ ) by liquefaction of CO at low temperature under pressure

(b) water gas by oxidation of CO into  $\text{CO}_2$  (by steam) which can be easily removed by dissolving in  $\text{H}_2\text{O}$

(c) electrolysis of water

(d) all the above methods

40. Out of the following metals which will give  $\text{H}_2$  on reaction with NaOH

I : Zn, II : Mg, III : Al, IV : Be

(a) I, II, III, IV

(b) I, III, IV

(c) II, IV

(d) I, III

41. Choose correct statement(s).

(a)  $\text{H}_2$  is more rapidly adsorbed on to surfaces than  $\text{D}_2$

(b)  $\text{H}_2$  reacts over 13 times faster with  $\text{Cl}_2$  than  $\text{D}_2$  because  $\text{H}_2$  has a lower energy of activation

(c) Both (a) and (b) are true

(d) None of the above is true

42. Abundance of  $\text{H}_2$  in the earth's atmosphere is very small. This is because

(a) the earth's gravitation field is too small to hold so light an element

(b)  $\text{H}_2$  exists in *ortho* and *para* form

(c)  $\text{H}_2$  is diatomic gas

(d)  $\text{H}_2$  is not the metal

43.  $\text{H}_2$  reacts much faster with  $\text{Cl}_2$  than  $\text{D}_2$ , because

(a) rate of diffusion of  $\text{H}_2$  is greater than  $\text{D}_2$

(b)  $\text{H}_2$  has lower energy of activation than  $\text{D}_2$

(c) both (a) and (b) are correct

(d) none of the statements is correct

44. Which is true statement about  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$ ?

(a)  $\text{D}_2\text{O}$  has lower dielectric constant than  $\text{H}_2\text{O}$

(b) NaCl is more soluble in  $\text{D}_2\text{O}$  than in  $\text{H}_2\text{O}$

(c) Both (a) and (b) are correct

(d) None of the above is correct

45. Out of  $\text{LiH}$ ,  $\text{MgH}_2$  and  $\text{CuH}$

(a) all are ionic hydrides

(b)  $\text{LiH}$ ,  $\text{MgH}_2$  are ionic and  $\text{CuH}$  covalent hydride

(c) all are covalent hydrides

(d)  $\text{LiH}$  is ionic,  $\text{MgH}_2$  and  $\text{CuH}$  are intermediate hydrides

46. There are three isotopes of hydrogen and three naturally occurring isotopes of oxygen ( ${}^{16}\text{O}$ ,  ${}^{17}\text{O}$  and  ${}^{18}\text{O}$ ). How many kinds of water are possible?

(a) 18

(b) 16

(c) 8

(d) 9

47. In the following compounds H is covalent bonded in case of

(a)  $\text{BaH}_2$

(b)  $\text{CaH}_2$

(c)  $\text{SiH}_4$

(d) NaH

48. Which of the following disproportionates when treated with water?

- (a)  $\text{SO}_3$  (b)  $\text{F}_2$   
(c)  $\text{N}_2$  (d)  $\text{Cl}_2$

49. Select the correct statement.

- (a) Ammonia is more soluble in aqueous ammonium chloride than in pure water.  
(b) Solid ammonium fluoride and ice are miscible in all proportions.  
(c) Both (a) and (b) are correct  
(d) None of the above statements is correct

50. H, D and T (isotopes of hydrogen) have nuclear spin quantum number respectively as

- (a)  $\frac{1}{2}, 1, \frac{1}{2}$  (b)  $\frac{1}{2}, \frac{1}{2}, 1$   
(c)  $\frac{1}{2}, 1, \frac{3}{2}$  (d)  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

51.  $\text{D}_2\text{O}$  has maximum density at

- (a)  $4^\circ\text{C}$  (b)  $11.6^\circ\text{C}$   
(c)  $0^\circ\text{C}$  (d)  $0\text{ K}$

52.  $\text{H}_2\text{O}_2$  is the hydride of

- (a)  $\text{O}_2$  (b)  $\text{H}_2\text{O}$   
(c) both (a) and (b) (d) none of these

53.  $\text{H}_2\text{O}_2$  can also be obtained by the partial oxidation of 2-propanol.



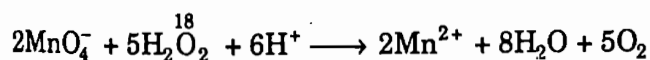
Intermediate in this reaction is

- (a)  $(\text{CH}_3)_2\text{C} \begin{array}{l} \text{OH} \\ \text{OH} \end{array}$   
(b)  $(\text{CH}_3)_3\text{C}^\cdot$   
(c)  $(\text{CH}_3)_2\text{C} \begin{array}{l} \text{OH} \\ \text{O}-\text{O}-\text{H} \end{array}$   
(d) none of the above

54.  $\text{H}_2\text{O}_2$  exists as ..... in alkaline medium.

- (a)  $\text{HO}_2^-$  (b)  $\text{HO}_2^\oplus$   
(c)  $\text{O}_2^{2-}$  (d)  $\text{H}_2\text{O}^\oplus$

55. In the following reaction using  $\text{H}_2^{18}\text{O}_2$ ,



$^{18}\text{O}$  goes with

- (a)  $\text{H}_2\text{O}$  (b)  $\text{O}_2$   
(c) both (a) and (b) (d) none of these

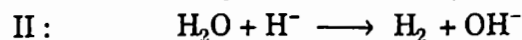
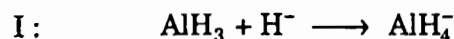
56. Water gas is a mixture of

- (a)  $\text{CO}$  and  $\text{H}_2\text{O}$  (b)  $\text{CO}$  and  $\text{N}_2$   
(c)  $\text{CO}$  and  $\text{H}_2$  (d)  $\text{CO}$  and  $\text{CH}_4$

57.  $\text{H}^-$  is a

- (a) Lewis base (b) Lowry-Bronsted base  
(c) both (a) and (b) (d) None of these

58. Consider following reactions



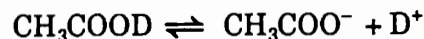
Select correct statements based on these reactions.

- (a)  $\text{H}^-$  is a Lewis acid in I and Lewis base in II  
(b)  $\text{H}^-$  is a Lewis base in I and Bronsted base in II  
(c)  $\text{H}^-$  is a Lewis acid in I and Bronsted acid in II  
(d)  $\text{H}^-$  is a Lewis base in I and II

59. Consider following statements :

I : Rate of transfer of  $\text{D}^+$  from  $\text{D}_2\text{O}$  is slower than that of  $\text{H}^+$  from  $\text{H}_2\text{O}$

II :  $K_a$  for  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$  is smaller than that of  $K_a$  for



III : Tritium is a radioactive isotope.

Select correct statements

- (a) I, II (b) II, III  
(c) I, III (d) I, II, III

60. Which is hydrolysis reaction?

- (a)  $\text{O}^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{OH}^-(\text{aq})$   
(b)  $\text{O}_2^{2-}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 4\text{OH}^-(\text{aq})$   
(c)  $4\text{O}_2^{2-}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow 3\text{O}_2(\text{g}) + 4\text{OH}^-(\text{aq})$   
(d) All of the above

61. The hydride ion  $\text{H}^-$  is stronger base than its hydroxide ion  $\text{OH}^-$ . Which of the following reactions will occur if sodium hydride ( $\text{NaH}$ ) is dissolved in water?

- (a)  $2\text{H}^+(\text{aq}) \longrightarrow \text{H}_2 + 2\text{e}^-$   
(b)  $\text{H}^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{OH}^- + \text{H}_2$   
(c)  $\text{H}^- + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{No reaction}$   
(d) None of the above

62. Permanent hardness of water can be removed by adding

- (a)  $\text{NaHCO}_3$  (b)  $\text{Na}_2\text{CO}_3$   
(c)  $\text{CaOCl}_2$  (d)  $\text{Cl}_2$

63. The correct decreasing order of basic strength is

- (a)  $\text{AsH}_3 > \text{SbH}_3 > \text{PH}_3 > \text{NH}_3$   
(b)  $\text{SbH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{NH}_3$   
(c)  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$   
(d)  $\text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{NH}_3$

64. Which statement is not correct for hydrogen?

- (a) It has a very high ionisation potential  
(b) It is always collected at cathode  
(c) It can form bonds in +1 as well as -1 oxidation state  
(d) It has same electronegativity as halogens

65. The most stable is

- (a)  $\text{NaH}$  (b)  $\text{RbH}$   
(c)  $\text{KH}$  (d)  $\text{LiH}$

66.  $\text{H}_2\text{O}_2$  is a reducing agent in the reaction  
 (a)  $\text{Ag}_2\text{O} + \text{H}_2\text{O}_2 \longrightarrow 2\text{Ag} + \text{H}_2\text{O} + \text{O}_2$   
 (b)  $2\text{KI} + \text{H}_2\text{O}_2 \longrightarrow 2\text{KOH} + \text{I}_2$   
 (c)  $\text{H}_2\text{O}_2 + \text{SO}_2 \longrightarrow \text{H}_2\text{SO}_4$   
 (d)  $\text{PbS} + 4\text{H}_2\text{O}_2 \longrightarrow \text{PbSO}_4 + 4\text{H}_2\text{O}$
67. Which cannot be oxidised by  $\text{H}_2\text{O}_2$  ?  
 (a)  $\text{Na}_2\text{SO}_3$  (b)  $\text{PbS}$   
 (c)  $\text{KI}$  (d)  $\text{O}_3$
68. Dil.  $\text{H}_2\text{SO}_4$  and oxide react to produce hydrogen peroxide. The oxide is  
 (a)  $\text{MnO}_2$  (b)  $\text{PbO}_2$   
 (c)  $\text{TiO}_2$  (d)  $\text{Na}_2\text{O}_2$
69. Heavy water is  
 (a) water at  $4^\circ\text{C}$   
 (b) water containing heavy ions  
 (c)  $\text{D}_2\text{O}$   
 (d) water containing sulphate of Ca
70. Adsorbed hydrogen by palladium is known as  
 (a) nascent (b) atomic  
 (c) heavy (d) occluded
71. Pure water can be obtained from sea water by  
 (a) centrifugation (b) plasmolysis  
 (c) reverse osmosis (d) sedimentation
72. Zn gives  $\text{H}_2$  gas with  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  but not with  $\text{HNO}_3$  because  
 (a) Zn acts as an oxidising agent when reacts with  $\text{HNO}_3$   
 (b)  $\text{HNO}_3$  is weaker acid than  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$   
 (c) in electrochemical series Zn is above hydrogen  
 (d)  $\text{NO}_3^-$  is reduced in preference to hydronium ion
73. Mass of one atom is  $6.66 \times 10^{-23}$  g. Its percentage in an hydride is 95.24. Thus, hydride is  
 (a)  $\text{MH}$  (b)  $\text{MH}_2$   
 (c)  $\text{MH}_3$  (d)  $\text{MH}_4$
74. On burning hydrogen in air, the colour of flame is  
 (a) green (b) light bluish  
 (c) yellow (d) none of these
75. Triple point of water is  
 (a) 273.16 K (b) 373.15 K  
 (c) 203.12 K (d) 193.16 K
76. Hydrogen can be fused to form helium at  
 (a) high temperature and high pressure  
 (b) high temperature and low pressure  
 (c) low temperature and high pressure  
 (d) low temperature and low pressure
77. Water gas is produced by  
 (a) passing steam over red hot coke  
 (b) passing steam and air over red hot coke  
 (c) burning coke in excess of air  
 (d) burning coke in limited supply of air
78. Hydrogen is produced by the reaction  
 (a)  $\text{Na}_2\text{O}_2 + 2\text{HCl}$  (b)  $\text{Mg} + \text{H}_2\text{O}$   
 (c)  $\text{BaO}_2 + \text{HCl}$  (d)  $\text{H}_2\text{S}_4\text{O}_8 + \text{H}_2\text{O}$
79. Which metal gives hydrogen gas on heating with hot concentrated alkali?  
 (a) Ag (b) Ni  
 (c) Zn (d) Cu
80. Hydrogen peroxide is prepared in the laboratory by  
 (a) passing  $\text{CO}_2$  into  $\text{BaO}_2$   
 (b) adding  $\text{MnO}_2$  to dil.  $\text{H}_2\text{SO}_4$   
 (c) adding  $\text{Na}_2\text{O}_2$  to cold water  
 (d) adding  $\text{PbO}_2$  into  $\text{KMnO}_4$
81. The hardness of water is estimated by  
 (a) EDTA method (b) titrimetric method  
 (c) conductivity method (d) distillation method
82. Hydrogen peroxide is reduced by  
 (a) ozone  
 (b) barium peroxide  
 (c) acidic solution of  $\text{KMnO}_4$   
 (d) lead sulphide suspension
83. Hard water is not fit for washing clothes because  
 (a) it contains impurities  
 (b) it is acidic in nature  
 (c) it gives precipitate with soap  
 (d) it contains  $\text{Na}_2\text{SO}_4$  and  $\text{KCl}$
84. The acid, not suitable for the preparation of hydrogen by the action of metals, is  
 (a)  $\text{HCl}$  (b)  $\text{CH}_3\text{COOH}$   
 (c)  $\text{HNO}_3$  (d)  $\text{H}_2\text{SO}_4$
85. Maximum number of hydrogen bonding in  $\text{H}_2\text{O}$  is  
 (a) 1 (b) 2  
 (c) 3 (d) 4
86.  $\text{Ag}_2\text{O} + \text{H}_2\text{O}_2 \longrightarrow 2\text{Ag} + \text{H}_2\text{O} + \text{O}_2$   
 In an above reaction  $\text{H}_2\text{O}_2$  acts as a/an  
 (a) oxidising agent (b) reducing agent  
 (c) bleaching agent (d) None of these
87. Ionic hydride reacts with water to give  
 (a) hydride ions (b) acidic solution  
 (c) protons (d) basic solutions
88.  $\text{H}_2\text{O}_2$  is manufactured these days by  
 (a) the action of  $\text{H}_2\text{SO}_4$  on  $\text{BaO}_2$   
 (b) the action of  $\text{H}_2\text{SO}_4$  on  $\text{Na}_2\text{O}_2$   
 (c) electrolysis of 50%  $\text{Na}_2\text{O}_2$   
 (d) burning hydrogen in excess oxygen
89. Which of the following is heavy water?  
 (a)  $\text{H}_2\text{O}^{18}$  (b)  $\text{H}_2\text{O}^{16}$   
 (c)  $\text{H}_2\text{O}_3$  (d)  $\text{D}_2\text{O}$
90. The volume of oxygen liberated at NTP from 15 mL of 20 volume  $\text{H}_2\text{O}_2$  is  
 (a) 250 mL (b) 300 mL  
 (c) 150 mL (d) 200 mL

91. Spin isomerism is shown by  
 (a) dichloro benzene (b) hydrogen  
 (c) dibasic acid (d) *n*-butane
92. Select incorrect statement.  
 (a) *Ortho* and *para* hydrogen are different due to difference in their nuclear spins  
 (b) *Ortho* and *para* hydrogen are different due to difference in their electron spins  
 (c) *Para* hydrogen has a lower internal energy than that of *ortho* hydrogen  
 (d) *Para* hydrogen is more stable at lower temperature
93.  $\text{SiH}_4$  is an example of which of the following type of hydrides  
 (a) ionic (b) interstitial  
 (c) metallic (d) covalent
94. Molar ratio of  $\text{H}_2\text{O}_2$  oxidised by one mole of  $\text{MnO}_4^-$  in basic and acidic medium is  
 (a) 1:1 (b) 1:2  
 (c) 3:5 (d) 5:3
95. Electrolysis of aqueous  $\text{NaCl}$  and  $\text{NaH}$  differs in  
 (a) formation of basic solution at the cathode by  $\text{NaCl}$  only  
 (b) formation of basic solution at the cathode by  $\text{NaH}$  only  
 (c) formation of  $\text{H}_2$  gas at cathode and anode both by  $\text{NaH}$  only  
 (d) formation of  $\text{H}_2$  gas at cathode and anode both by  $\text{NaCl}$  only
96. Select correct statement(s).  
 (a) Hydride ion is larger than any of the halide ions except iodide  
 (b) Hydrides ions are reducing agents  
 (c) Boranes are electron deficient hydrides  
 (d) All of the above are correct statements
97. Metallic hydrides  
 (a) are also called interstitial hydrides  
 (b) are non-stoichiometric, being deficient in hydrogen  
 (c) are poor conductors of electricity, exhibit less paramagnetism and have hydrogen as atom and not as molecule  
 (d) have all the properties given above
98. Hydride ion is a  
 (a) strong conjugate acid of  $\text{H}_2$   
 (b) strong conjugate base of  $\text{H}_2$   
 (c) strong conjugate acid of  $\text{H}^+$   
 (d) strong conjugate base of  $\text{H}^+$
99. Select incorrect statement.  
 (a)  $\text{H}^+$  can exist as  $\text{H}_9\text{O}_4^+$  in water  
 (b)  $\text{H}_2$  is thermally stable  
 (c) Ionisation of  $\text{CH}_3\text{COOH}$  is slower than that of  $\text{CH}_3\text{COOD}$   
 (d) Kinetic isotopic effect is observed when there is retardation in the rate water  $\text{H}_2\text{O}$  is replaced by  $\text{D}_2\text{O}$ .
100.  $\text{H}_2$ ,  $\text{D}_2$  and  $\text{T}_2$  do not differ in  
 (a) freezing point (b) boiling point  
 (c) critical temperature (d) bond energy
101.  $\text{H}_2\text{O}_2$  is present as ..... in acidic medium.  
 (a)  $\text{HO}_2^-$  ion (b)  $\text{H}_3\text{O}_2^+$  ion  
 (c)  $\text{H}^+$  ion (d)  $\text{O}_2^{2-}$  ion
102. Hydroxyl radicals are used in organic reactions. These are obtained from  
 (a) glycol (b) glycerol  
 (c)  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  (d)  $\text{H}_2\text{O}_2/\text{Fe}^{3+}$
103.  $\text{H}_2\text{O}_2$  is a reducing agent as shown by  
 (a)  $\text{H}_2\text{O}_2 \longrightarrow 2\text{H}^+ + \text{O}_2 + 2\text{e}^-$   
 (b)  $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow 2\text{H}_2\text{O}$   
 (c)  $\text{H}_2\text{O}_2 \longrightarrow \text{H}^+ + \text{HO}_2^-$   
 (d)  $\text{H}_2\text{O}_2 + \text{H}^+ \longrightarrow \text{H}_3\text{O}_2^+$
104. Industrial source of  $\text{H}_2\text{O}_2$  is  
 (a) by oxidation of 2-ethyl anthraquinol in a cyclic process  
 (b) by partial oxidation of 2-propanol  
 (c) by both (a) and (b)  
 (d) none of the above
105. Fuel used for rocket propulsion is a mixture of  
 (a) hydrazine and hydrogen peroxide  
 (b) hydrazine and TNT  
 (c) hydroxyl amine and TNT  
 (d) hydroxyl amine and hydrogen peroxide
106. Select correct statement(s).  
 (a)  $\text{H}_2\text{O}_2$  reduces  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$  in acidic medium  
 (b)  $\text{H}_2\text{O}_2$  reduces  $\text{MnO}_4^-$  to  $\text{MnO}_2$  in basic medium  
 (c)  $\text{H}_2\text{O}_2$  can be used to bleach blackened oil paintings  
 (d) All the above are correct statement
107. Electron-deficient hydride is/are  
 (a)  $\text{BH}_3$  (b)  $\text{AlH}_3$   
 (c)  $\text{BeH}_2$  (d) all of these
108. Perhydrol is  
 (a) 30% solution of  $\text{H}_2\text{O}_2$   
 (b) "100 volume"  $\text{H}_2\text{O}_2$   
 (c) both (a) and (b) are correct  
 (d) none of the above is correct
109. 10 mL of  $\text{H}_2\text{O}_2$  solution on treatment with KI and titration of liberated  $\text{I}_2$ , required 10 mL of 1 N hypo. Thus  $\text{H}_2\text{O}_2$  is  
 (a) 1N (b) 5.6 volume  
 (c)  $17 \text{ gL}^{-1}$  (d) all are correct
110. In alkaline  $\text{H}_2\text{O}_2$   
 (a)  $\text{Mn}^{2+}$  changes to  $\text{MnO}_2$   
 (b)  $\text{Cr}^{3+}$  changes to  $\text{CrO}_4^{2-}$   
 (c) both (a) and (b) are correct  
 (d) none of the above is correct

## One or More Than One Options Correct

- Select correct statements.
  - Boiling point of  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{HF}$  are maximum in their respective group due to intermolecular H-bonding
  - Boiling point of  $\text{CH}_4$  out of  $\text{CH}_4$ ,  $\text{SiH}_4$ ,  $\text{GeH}_4$  and  $\text{SnH}_4$  is least due to lack of H-bonding
  - Benzoic acid forms dimer by H-bonding
  - $\text{H}_2\text{O}$  exists as  $\text{H}_9\text{O}_4^+$  in acidic medium
- $\text{H}_2\text{O}_2$  can be obtained when following reacts with  $\text{H}_2\text{SO}_4$  except with
  - $\text{PbO}_2$
  - $\text{BaO}_2$
  - $\text{Na}_2\text{O}_2$
  - $\text{SrO}_2$
- How does  $\text{H}_2\text{O}_2$  differ from  $\text{O}_3$  in its chemical action?
  - In oxidising  $\text{PbS}$  to  $\text{PbSO}_4$
  - In liberating  $\text{I}_2$  from  $\text{KI}$
  - In decolourising acidified  $\text{KMnO}_4$
  - In oxidising  $\text{K}_4[\text{Fe}(\text{CN})_6]$  to  $\text{K}_3[\text{Fe}(\text{CN})_6]$
- Which of the following statements about  $\text{H}_2\text{O}_2$  are true?
  - $\text{H}_2\text{O}_2$  is used to clean oil paintings
  - $\text{H}_2\text{O}_2$  acts as oxidising as well as reducing agent
  - Two hydroxyl groups in  $\text{H}_2\text{O}_2$  lie in the same plane
  - It retains same structure in liquid and solid form
- $\text{H}^+$ ,  $\text{D}^+$  and  $\text{T}^+$  differ in all except in
  - number of electrons
  - number of neutrons
  - ionic mass
  - electronic configuration
- Which is/are radioactive isotope(s) of hydrogen?
  - ${}^1_1\text{H}$
  - ${}^2_1\text{H}$
  - ${}^3_1\text{H}$
  - ${}^4_1\text{H}$
- Which is a source of nascent hydrogen?
  - $\text{Zn} + \text{dil. HCl}$ ,
  - $\text{CH}_3\text{OH} + \text{Na}$
  - Electrolysis of  $\text{H}_2\text{O}$
  - Silent electric discharge
- Select correct statement(s) about lime light
  - Oxy-hydrogen flame
  - Used in welding
  - Temperature of lime light is sufficient to melt even platinum
  - Produced in an endothermic reaction
- "10 volume"  $\text{H}_2\text{O}_2$  means
  - 1 mL  $\text{H}_2\text{O}_2$  gives 10 mL  $\text{O}_2$  at NTP
  - 1 g  $\text{H}_2\text{O}_2$  gives 10 mL  $\text{O}_2$  at NTP
  - 1 mol  $\text{H}_2\text{O}_2$  gives 10 mL  $\text{O}_2$  at NTP
  - 10 mL gives 1 mol  $\text{H}_2$  and 1 mol  $\text{O}_2$  at NTP
- Industrially  $\text{H}_2\text{O}_2$  is obtained from
  - 2-ethyl anthraquinol by oxidation and then reduction in a cyclic process
  - $\text{H}_2\text{SO}_5$
  - $\text{H}_2\text{S}_2\text{O}_8$
  - $\text{BaO}_2$
- Density of  $\text{H}_2\text{O}$  is maximum at
  - $0^\circ\text{C}$
  - $100^\circ\text{C}$
  - $-273^\circ\text{C}$
  - $4^\circ\text{C}$
- Temporary hardness and permanent hardness can be removed respectively by addition of
  - $\text{CaO}$ ,  $\text{CaCO}_3$
  - $\text{CaO}$ ,  $\text{Na}_2\text{CO}_3$
  - $\text{Na}_2\text{CO}_3$ ,  $\text{CaO}$
  - $\text{NaHCO}_3$ ,  $\text{CaCl}_2$
- Decomposition of  $\text{H}_2\text{O}_2$  can be prevented by addition of
  - ferrous sulphate
  - oxalic acid
  - ozone
  - glycerol
- Which is/are true statement(s)?
  - The layer of ice on the surface of river in the winter acts as a thermal insulator between the water below and the air above
  - The fish and other marine organisms are enabled to survive long periods of freezing weather due to the fact that ice is lighter than water
  - When ice is formed volume decreases
  - Density of ice is maximum at  $0^\circ\text{C}$
- Hydrides of metals are named like
  - alkane
  - alkene
  - alkyne
  - none is correct
- In water, or in aqueous solutions of  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ , proton exists as
  - $\text{H}_3\text{O}^+$
  - $\text{H}(\text{H}_2\text{O})_4^+$
  - $\text{H}(\text{H}_2\text{O})_n^+$
  - $[\text{H}_3\text{O}^+][\text{OH}^-]$
- $\text{H}_2\text{O}_2$  is "5.6 volume", then
  - it is 1.7% weight by volume
  - it is 1 N
  - it is 1 M
  - it is 5.6 M
- $\text{H}_2$  can be obtained from
  - water gas ( $\text{CO} + \text{H}_2$ ) by liquefaction of  $\text{CO}$  at low temperature under pressure
  - water gas by oxidation of  $\text{CO}$  into  $\text{CO}_2$  (by steam) which can be easily removed by dissolving in  $\text{H}_2\text{O}$
  - electrolysis of water or  $\text{NaOH}$
  - reaction of  $\text{NaOH}$  on  $\text{Zn}$
- Out of the following metals which will give  $\text{H}_2$  on reaction with  $\text{NaOH}$   
I :  $\text{Zn}$ , II :  $\text{Mg}$ , III :  $\text{Al}$ , IV :  $\text{Be}$ 
  - I, II, III, IV
  - I, III, IV
  - II, IV
  - I, III

20. Which is hydrolysis reaction?

- (a)  $O^{2-}(aq) + H_2O(l) \longrightarrow 2OH^-(aq)$   
 (b)  $O_2^{2-}(aq) + 2H_2O(l) \longrightarrow O_2(g) + 4OH^-(aq)$   
 (c)  $4O_2^{2-}(aq) + 2H_2O(l) \longrightarrow 3O_2(g) + 4OH^-(aq)$   
 (d)  $Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+$

## Brain Twisters

- How many grams of barium hydride must be treated with water to obtain 4.36 L of hydrogen at 20°C and 0.975 atm pressure? (Ba = 137).
- An element *X* reacts with  $H_2$  gas at 200°C to form compound *Y*. When *Y* is heated to a higher temperature, it decomposes to the element *X* and  $H_2$  gas in the ratio of 559 mL of  $H_2$  (measured at STP) for 1.00 g of *X* reacted. *X* also combines with  $Cl_2$  to form a compound *Z*, which contains 63.89 per cent by mass of chlorine. Deduce the identify of *X*, *Y* and *Z*.
- $H_2O_2$  is reduced rapidly by  $Sn^{2+}$ .  $H_2O_2$  decomposes slowly at room temperature to yield  $O_2$  and  $H_2O$ . Calculate the volume of  $O_2$  gas produced at 20°C and 1 atm when 200 g  $H_2O_2$  having 10% by mass  $H_2O_2$  is treated with 100 mL of 2.00 M  $Sn^{2+}$  and then the mixture is allowed to stand until no further reaction occurs.
- $H_2O_2$  is marked "22.4 volume". How much of it (in mL) are required to oxidise 3.4 g  $H_2S$  gas?
- A 'hair-bleach' solution contains  $H_2O_2$ . The amount of  $H_2O_2$  in a 12.5 g sample was determined by titration with  $KMnO_4$  in acidic solution. If 39.3 mL of 0.5045 N  $KMnO_4$  was required, how many equivalents of  $H_2O_2$  are contained in the solution? What is the mass percentage of  $H_2O_2$  in the bleach solution?
- A 1.84 g sample of an alkaline-earth metal hydride was treated with an excess of dil. HCl and the resulting gas was collected in 1.0 L container at 20°C. The measured pressure of the gas was 750.0 mmHg. Identify the alkaline earth-metal.
- A 5.0 mL of  $H_2O_2$  solution liberates 0.508 g  $I_2$  from an acidified KI solution. Calculate volume strength of  $H_2O_2$  solution.

## Passage Comprehension Questions

### Passage 1

Read the following experiments and answer the questions at the end of it.

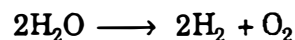
"Research scholar *A* added zinc pieces into aqueous  $FeCl_3$  solution and performed some experiments with resultant solution." Research scholar *B* passed  $H_2$  gas into aqueous  $FeCl_3$  solution and performed some experiments with resultant solution."

- Yellow coloured  $FeCl_3$  solution changed to light green (appeared as colourless) in the experiment of  
 (a) *A* (b) *B*  
 (c) both of these (d) none of these
- Select correct statements.  
 (a) Zn pieces liberate nascent hydrogen on reaction with acidic solution of  $FeCl_3$   
 (b)  $FeCl_3$  solution is reduced to  $FeCl_2$  in the experiments of *A* and *B* both  
 (c) Blue colour complex is formed in both the experiments on reaction with  $K_4[Fe(CN)_6]$   
 (d) A blood red colour is formed on reaction with KCNS in experiment *B*

### Passage 2

Depletion of resources of fossil fuels will at some future time make hydrogen, either for use directly by combustion and electrochemically in fuel cells or indirectly *via* hydrogenation of coal, the major alternative to nuclear energy; hence, arises the current interest in the so-called **hydrogen economy**.

A thermochemical cycle for hydrogen production involves at least one element that can exist in two different oxidation states.



Read the above passage and answer the following questions.

- Production of  $H_2$  from  $H_2O$  requires a net input of energy that would come from  
 (a) nuclear source (b) solar source  
 (c) both of these (d) None of these
- In the above thermochemical cycle,  $FeCl_2$  is one of the catalyst involved and thus regenerated at the end of the reaction, after formed into  
 (a)  $FeCl_3, FeO, Fe_2O_3$  (b)  $FeCl_3, Fe_2O_3, Fe_3O_4$   
 (c)  $FeCl_3, FeO$  (d)  $FeCl_3, Fe_3O_4$
- $H_2$  is produced in the following thermochemical reaction  
 (a)  $FeCl_2 + H_2O \longrightarrow$   
 (b)  $Fe_3O_4 + Cl_2 + HCl \longrightarrow$   
 (c)  $FeO + H_2O \longrightarrow$   
 (d)  $FeCl_3 + H_2O \longrightarrow$

## Assertion & Reason

Codes :

- (a) Both *A* and *R* are true and *R* is the correct explanation of *A*.  
 (b) Both *A* and *R* are true but *R* is not the correct explanation of *A*.  
 (c) *A* is true but *R* is false.  
 (d) *A* is false but *R* is true.  
 (e) *A* and *R* both are false.

**1. Assertion (A) :** On adding zinc pieces to  $\text{FeCl}_3(\text{aq})$  solution, colour changes from deep yellow to light green.

**Reason (R) :** Aqueous  $\text{FeCl}_3$  solution is acidic and on adding zinc, nascent hydrogen is produced which reduces deep yellow  $\text{FeCl}_3$  solution to light green  $\text{FeCl}_2$  solution.

**2. Assertion (A) :** On passing  $\text{H}_2$  gas into aqueous  $\text{Fe}^{3+}$  solution, resulting solution gives test of  $\text{Fe}^{3+}$ .

**Reason (R) :**  $\text{H}_2(\text{g})$  reduces  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  but  $\text{Fe}^{2+}$  is oxidised to  $\text{Fe}^{3+}$  by atmospheric oxygen.

**3. Assertion (A) :** Drinking of heavy water ( $\text{D}_2\text{O}$ ) mixed water ( $\text{H}_2\text{O}$ ) could prove fatal.

**Reason (R) :** There is slower rate of transfer of  $\text{D}^+$  compared with that of  $\text{H}^+$  ion in acid-base reactions involved in enzyme catalysis.

**4. Assertion (A) :** Ionisation constant of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COOD}$  are very equal.

**Reason (R) :** The kinetic isotopic effect is not observed in the ionisation of weak acid.

**5. Assertion (A) :** In space crafts  $\text{H}_2$  gas is used in fuel cells for generating electrical energy and for providing clean drinking water to the astronauts.

**Reason (R) :** A fuel cell may have an alkaline or acidic electrolyte.

**6. Assertion (A) :** Hydride ( $\text{H}^-$ ) is a conjugate base of hydrogen ( $\text{H}_2$ ).

**Reason (R) :** Every negative ion is an electron-pair donor and is thus, a Lewis base.

**7. Assertion (A) :** Ionic hydrides are the ready-made source of  $\text{H}_2$ .

**Reason (R) :**  $\text{LiH}$  is an ionic hydride.

**8. Assertion (A) :**  $\text{H}_2\text{O}_2$  decomposes  $\text{Na}_2\text{CO}_3$  to give  $\text{CO}_2$ .

**Reason (R) :**  $\text{H}_2\text{O}_2$  has two protons and is thus a strong acid.

**9. Assertion (A) :** When blood is added to a solution of  $\text{H}_2\text{O}_2$ , the solution bubbles furiously.

**Reason (R) :** Catalase (an enzyme) present in blood decomposes  $\text{H}_2\text{O}_2$  and produces bubbles of  $\text{O}_2$ .

**10. Assertion (A) :**  $\text{KO}_2$  is used as life supports in space crafts.

**Reason (R) :**  $\text{KO}_2$  absorbs  $\text{CO}_2$  and releases  $\text{O}_2$ .

## True & False

1.  $\text{KO}_2$  is used as life supports in space crafts, submarines and emergency breathing apparatus since it absorbs  $\text{CO}_2$  and releases  $\text{O}_2$ .

2.  $\text{O}_2$  is diamagnetic and  $\text{KO}_2$  is paramagnetic.

3. Peroxides and oxides are decomposed by  $\text{H}_2\text{O}$  forming  $\text{O}_2$  and their behaviour becomes alkaline.

4. Due to very small size of  $\text{H}^+$ , it has very high polarising power and therefore, distorts the electron-cloud on other atoms.

5.  $\text{H}^+$  exists as  $\text{H}_9\text{O}_4^+$ .

6. Ionic size of  $\text{H}$ ,  $\text{H}^+$  and  $\text{H}^-$  are equal.

7. Ionisation constant of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COOD}$  are same.

8. Spin isomerism is observed in  $\text{H}_2$ .

9. On electrolysis of  $\text{HCOONa}(\text{aq})$ ,  $\text{H}_2$  is obtained at cathode and anode both.

10. Ionic hydrides conduct electricity in fused state.

11. Hydride is a conjugate acid of  $\text{H}_2$ .

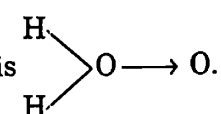
12. Hydride is a Lewis base.

13.  $\text{H}_2\text{O}_2$  is "10 volume" if 1 mL gives 10 mol  $\text{O}_2$ .

14.  $\text{H}_2\text{O}_2$  behaves as an acid, oxidising agent and reducing agent.

15.  $\text{H}_2\text{O}_2$  is used as fuel for rockets.

16.  $\text{H}_2\text{O}_2$  oxidises  $\text{Cr}^{3+}$  to  $\text{CrO}_4^{2-}$  in basic medium.

17. True structure of  $\text{H}_2\text{O}_2$  is 

18. Catalase present in blood interacts with  $\text{H}_2\text{O}_2$  forming  $\text{O}_2$ .

19. Density of  $\text{H}_2\text{O}$  is not affected by change in temperature.

20. Tritium is the radioactive isotope of hydrogen.

## Fill in the Blanks

1. Aqueous solution of ..... on electrolysis gives  $\text{H}_2$  at anode and cathode both.

2. .... and ..... are two spin isomers of  $\text{H}_2$ .

3. At absolute zero there is only ..... form of  $\text{H}_2$ .

4. Different atomic masses of three isotopes of hydrogen is due to the difference in the number of .....

- Hydrogen resembles ..... metals in the formation of ..... cation and ..... elements in the formation of ..... anion.
- Hydrogen is the ..... most abundant element in the earth's crust.
- Water gas contains CO and .....
- Very pure  $H_2$  is obtained by electrolysis of .....
- $H_2$  is ..... rapidly adsorbed on to the surfaces than  $D_2$ .
- $H_2$  reacts over 13 times faster with  $Cl_2$  than  $D_2$ , because  $H_2$  has a ..... energy of activation.
- Auto-protolysis constant of  $H_2O$  is ..... times more than that of  $D_2O$ .
- Due to lower value of dielectric constant of  $D_2O$  than  $H_2O$ , ionic compounds are ..... soluble in  $D_2O$  than in  $H_2O$ .
- B.E. of O—D bond in  $D_2O$  is ..... than that of O—H bond in  $H_2O$ .
- ${}^6_3Li + {}^1_0n \longrightarrow {}^4_2He + \dots\dots\dots$
- When water is electrolysed,  $H_2$  is liberated much ..... than  $D_2$  and thus remaining water becomes enriched in .....
- Tritium is widely used as radioactive .....
- Considerable differences between the physical properties of *ortho* and *para* forms of  $H_2$  is because of differences in their ..... energy.
- $LiH$ ,  $NaH$ ,  $KH$  are some examples of ..... hydrides.
- Interstitial hydrides are made by ..... metals.
- $H_3O^+$  is .....  $H^+$  ion and can be written as .....

## Matrix-Match Type Questions

### I. One or More Correct

- Match the species in Column I with corresponding properties in Column II.

| Column I           | Column II                |
|--------------------|--------------------------|
| A. $H_2O$          | 1. Reducing agent        |
| B. $H_2O_2$        | 2. Oxidising agent       |
| C. Aqueous $Na_2O$ | 3. Paramagnetic          |
| D. Aqueous $KO_2$  | 4. Diamagnetic           |
| E. Aqueous $CaH_2$ | 5. Turns red litmus blue |
|                    | 6. Turns blue litmus red |

- Match the species in Column I with the corresponding properties in Column II.

| Column I    | Column II              |
|-------------|------------------------|
| A. $LiH$    | 1. Reducing agent      |
| B. $H_2O$   | 2. Lewis base          |
| C. $H_3O^+$ | 3. Conjugate base      |
| D. $BH_3$   | 4. Lewis acid          |
| E. $H$      | 5. Lowry Bronsted acid |
|             | 6. Lowry Bronsted base |

## Integer Answer Types

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the *ORS* have to be darkened. For example, if the correct answers to question number X, Y, Z and W (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will like the following

| X                       | Y                       | Z                       | W                       |
|-------------------------|-------------------------|-------------------------|-------------------------|
| <input type="radio"/> 0 | <input type="radio"/> 0 | <input type="radio"/> 0 | <input type="radio"/> 0 |
| <input type="radio"/> 1 | <input type="radio"/> 1 | <input type="radio"/> 1 | <input type="radio"/> 1 |
| <input type="radio"/> 2 | <input type="radio"/> 2 | <input type="radio"/> 2 | <input type="radio"/> 2 |
| <input type="radio"/> 3 | <input type="radio"/> 3 | <input type="radio"/> 3 | <input type="radio"/> 3 |
| <input type="radio"/> 4 | <input type="radio"/> 4 | <input type="radio"/> 4 | <input type="radio"/> 4 |
| <input type="radio"/> 5 | <input type="radio"/> 5 | <input type="radio"/> 5 | <input type="radio"/> 5 |
| <input type="radio"/> 6 | <input type="radio"/> 6 | <input type="radio"/> 6 | <input type="radio"/> 6 |
| <input type="radio"/> 7 | <input type="radio"/> 7 | <input type="radio"/> 7 | <input type="radio"/> 7 |
| <input type="radio"/> 8 | <input type="radio"/> 8 | <input type="radio"/> 8 | <input type="radio"/> 8 |
| <input type="radio"/> 9 | <input type="radio"/> 9 | <input type="radio"/> 9 | <input type="radio"/> 9 |

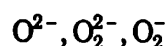
### Set I

- Number of neutrons in the heaviest isotopes of hydrogen is .....
- Number of peroxy linkage (s) in  $H_2S_2O_8$  is .....
- Two moles of  $MnO_4^-$  reduces  $x$  mole(s) of  $H_2O_2$  in basic medium.  $x$  is .....
- 68 g  $H_2O_2$  will make ..... equivalent(s).
- $H_2O_2$  is "33.6" volume. Thus, its normality is .....
- $CrO_5$  has peroxy linkage(s).  $x$  is .....
- How many moles of  $H_2O_2$  are oxidised by 2 moles of  $KMnO_4$  in acidic medium?
- 5.0 mL of  $H_2O_2$  solution liberates 1.016 g of  $I_2$  from an acidified KI solution. Thus, volume strength (at STP) is approximately .....

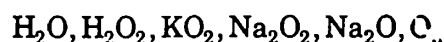


## Set II

- 1. How many of the following make alkaline solution in water?**

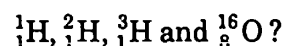


- 2. How many of the following are oxidant?**



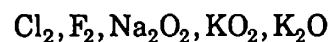
3. Ionic product,  $[H^+][HO_2^-]$  of  $H_2O_2$  was found to be  $1 \times 10^{-12}$  at a given temperature. Thus, pH of  $H_2O_2$  is .....

- 4. How many types of water can be formed out of**

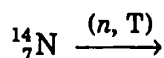


5.  $H_2$  is formed by electrolysis of aqueous brine solution. In an experiment 0.112 mL of  $H_2$  gas is formed at NTP. What is the pH after electrolysis of brine solution?

6. How many of the following undergo disproportionation when dissolved in water?



- 7.  ${}^{14}_7\text{N}$  undergoes nuclear reaction**



**What is atomic number of the atom formed?**

8. 5.6 g of a unsaturated hydrocarbon occupies 2.24 L at NTP. It also required 4.48 L of  $H_2$  gas for its reduction. How many  $\pi$  bonds does it have?

## Test Yourself on the Periodic Table

- 1. Look at the location of elements A, B, C and D in the following Periodic Table**

- Write the formula of the simplest binary hydride of each element.
- Classify each binary hydride as ionic, covalent or interstitial.
- Which of these hydrides are molecular?
- What is the oxidation state of the element in hydrides A, C and D?

- ## 2. Arrange the compounds of hydrogen with elements

- (a) *A, B, C, D* in increasing acid strength  
(b) *A, B, C, D* in increasing boiling point  
(c) *E, F, G, A* in increasing H-bonding strength

- 3. In the Periodic Table given below**

A grid of 100 squares arranged in a 10x10 pattern. The top row and the first column are shaded gray, representing the first 10 natural numbers (1 to 10) in a 10x10 grid.

**trace the element(s)**

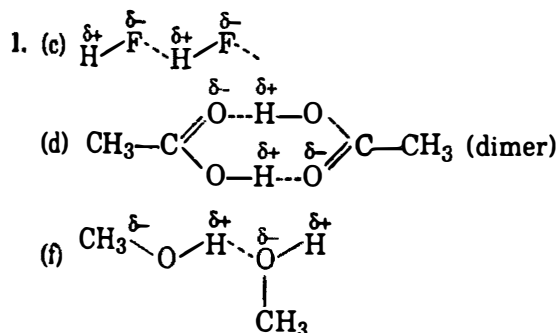
- (a) that has maximum dissociation energy in diatomic state  
(b) that forms double bond in diatomic state  
(c) that forms triple bond in diatomic state  
(d) that forms compounds with +1 oxidation state with hydrogen

# Answers & Solutions

## Master Exercises

### Exercise 1

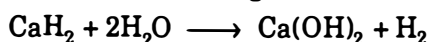
#### Short Answer Type Questions



2. Hydrogen is a non-metal in its natural gaseous state as well as in liquid state. If a very thin layer of liquid hydrogen (about 0.5 mm) placed in between two single-crystal alumina is subjected to shock compression under a very high pressure (about 2 million atmosphere), then liquid hydrogen behaves like metal and its conducting power is very comparable to Rb and Cs. This transition of a non-metal to a metal under very high pressure is called metallisation of hydrogen.

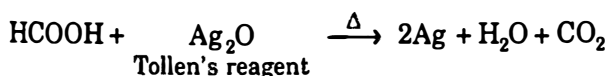
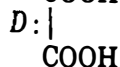
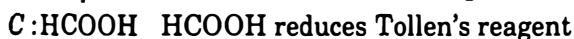
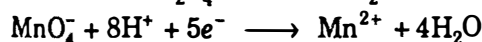
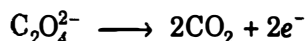
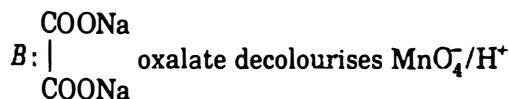
This phenomenon is taking place at the planet Jupiter.

3. Hydrides : LiH, BeH<sub>2</sub>, BH<sub>3</sub>
4. In aqueous solution, hydrides are decomposed by H<sub>2</sub>O forming which show reducing nature.

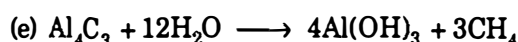
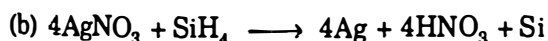


5. (a) boranes (b) silanes (c) alkanes (d) LiAlH<sub>4</sub>

6. A : HCOONa



7. (a)  $\text{SiCl}_4 + \text{Li[AlH}_4] \longrightarrow \text{SiH}_4 + \text{AlCl}_3 + \text{HCl}$



8.

| S. no. | Metallic hydride | Property                                       | Used as                                |
|--------|------------------|------------------------------------------------|----------------------------------------|
| 1.     | ZrH <sub>2</sub> | Low thermal neutron capture cross-section area | Moderation in nuclear reaction         |
| 2.     | TiH <sub>2</sub> | High neutron-capture cross-section area        | Shielding material in nuclear reaction |

#### Analytical Questions

1.  $\text{H}_2\text{O}_2 = 1 \text{ g (impure)} = \frac{x}{100} \text{ g pure}$

$$\text{Equivalent of H}_2\text{O}_2 = \frac{x}{100} \times \frac{1}{17}$$

Let normality of KMnO<sub>4</sub> = N

$\therefore \text{Equivalent of KMnO}_4 = \frac{Nx}{1000}$

$\therefore \frac{Nx}{1000} = \frac{x}{1700}$

$\therefore N = \frac{10}{17}$

2. Let normality of H<sub>2</sub>O<sub>2</sub> = N

$$\text{Equivalent of H}_2\text{O}_2 = \frac{5N}{1000} = \frac{N}{200}$$

$$\text{Equivalent of I}_2 = \frac{0.508}{127}$$

$$\text{Equivalent of H}_2\text{O}_2 = \frac{0.508}{127}$$

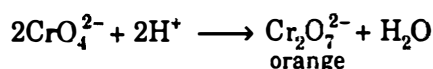
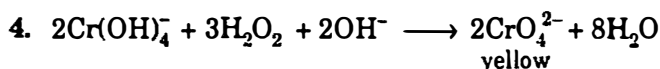
$\therefore \frac{N}{200} = \frac{0.508}{127} \Rightarrow N = 0.8 \text{ N H}_2\text{O}_2$

If volume strength = x

then  $N = \frac{x}{5.6}$

$\therefore x = N \times 5.6$   
 $= 0.8 \times 5.6 = 4.48 \text{ volume}$

3. (A) : H<sub>2</sub>O<sub>2</sub>; (B) : H<sub>2</sub>O

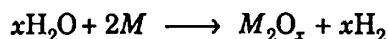


5. pH = 5.91

$\therefore [\text{H}^+] = 10^{-5.91} = 10^{-6} \times 10^{0.09} = 1.23 \times 10^{-6} \text{ M}$

$$\begin{aligned}
 [\text{HO}_2^-] &= 1.23 \times 10^{-6} \text{ M} \\
 \therefore K(\text{H}_2\text{O}_2) &= [\text{H}^+][\text{HO}_2^-] \\
 &= (1.23 \times 10^{-6})^2 \\
 &= 1.51 \times 10^{-12} \text{ M}^2
 \end{aligned}$$

6. React  $\text{H}_2\text{O}$  with a reducing agent to produce  $\text{H}_2$

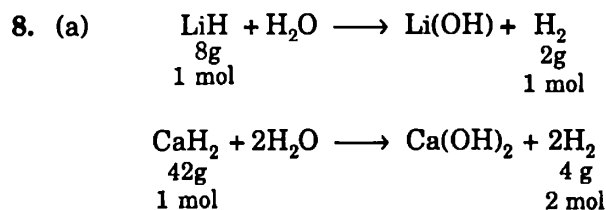


(b) Al and (d) Ca could be used

7. (a), (b), (d) are different kinds of water and have similar properties.

(c) and (e) are different kinds of hydrogen peroxides and have similar properties.

Properties of (a), (b) and (d) are quite different from those of (c) and (e).



$$8 \text{ g LiH gives } = 2 \text{ g H}_2$$

$$1 \text{ g LiH gives } = 0.25 \text{ g H}_2$$

$$42 \text{ g CaH}_2 \text{ gives } = 4 \text{ g H}_2$$

$$1 \text{ g CaH}_2 = 0.095 \text{ g.}$$

Thus, LiH

$$\begin{aligned}
 \text{(b)} \quad pV &= nRT \\
 n(\text{H}_2) &= \frac{pV}{RT} \\
 &= \frac{150 \times 100}{0.0821 \times 298} = 613.1 \text{ mol}
 \end{aligned}$$

$$2 \text{ mol H}_2 \text{ is obtained from } = 1 \text{ mol CaH}_2 = 42 \text{ g CaH}_2$$

$$\begin{aligned}
 \therefore 613.1 \text{ mol H}_2 \text{ is obtained from } &= \frac{42}{2} \times 613.1 \text{ g CaH}_2 \\
 &= 12875.1 \text{ g} \\
 &= 12.875 \text{ kg}
 \end{aligned}$$

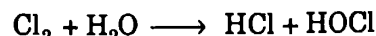
9. K is oxidised by water :



$\text{F}_2$  is reduced by water :



$\text{Cl}_2$  and  $\text{Br}_2$  disproportionate when treated with  $\text{H}_2\text{O}$



$$10. \text{ Moles of D}_2 = \frac{pV}{RT} = \frac{2 \times 0.9}{0.0821 \times 298} = 0.0736$$

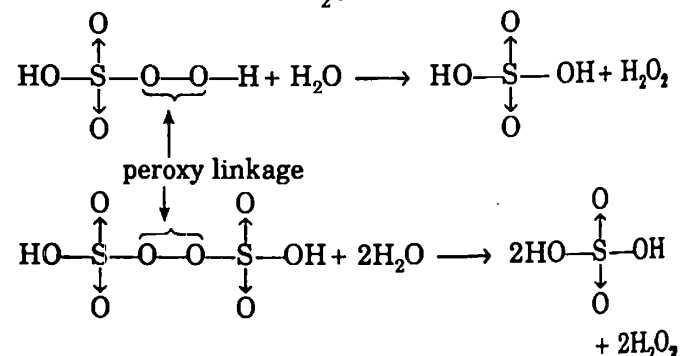
$$\therefore \text{H}_2\text{O} = 0.0736 \text{ mol} = 0.0736 \times 18 \text{ g} \quad ]$$

Actual water required with 0.015%  $\text{D}_2$  and 80% recovery

$$\begin{aligned}
 &= \frac{0.0736 \times 18}{\frac{0.015}{100} \times \frac{80}{100}} \\
 &= 11040 \text{ g} \\
 &= 11.040 \text{ kg}
 \end{aligned}$$

11. A :  $\text{CO}$ ; B :  $\text{H}_2$ ; C :  $\text{CO}_2$ ; D :  $\text{CaCO}_3$ ; E :  $\text{Ca(HCO}_3)_2$

12. A and B both are peroxo acids since,  $\text{H}_2\text{O}_2$  is formed due to their reactions with  $\text{H}_2\text{O}$ .



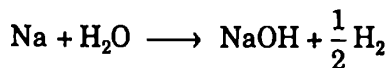
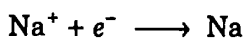
## Exercise 2

### Only One Option Correct

1. (c) Salt Ionisation

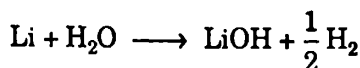
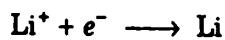


At cathode

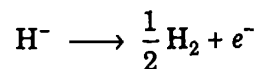
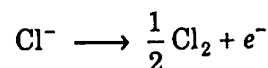
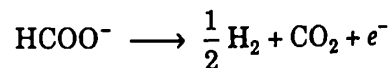
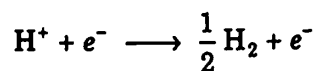


same

same

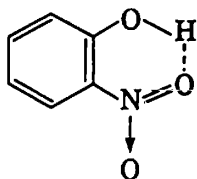


At anode



Thus, (c)

2. (a)  
 3. (c) Force of attraction is minimum thus most volatile  
 4. (a) *o*-nitrophenol has intramolecular H-bonding thus most volatile.



Thus, (a)

5. (d) 6. (d)

7. (a)  $\text{PbO}_2$  does not have peroxy linkage

Thus, (a)

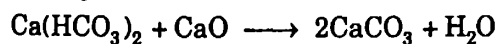
8. (a) 9. (b) 10. (d) 11. (c) 12. (b)

13. (c)  $\text{O}_3$  does not decolourise  $\text{KMnO}_4$

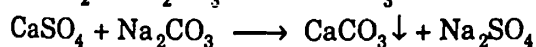
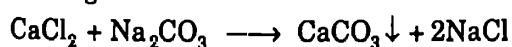
14. (c) 15. (d) 16. (b) 17. (a) 18. (a)

19. (d)

20. (b) Temporary hardness is due to dissolved  $\text{HCO}_3^-$  of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$

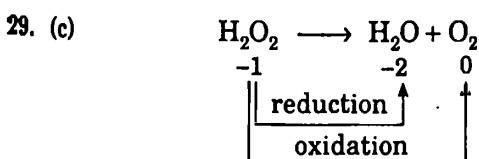


Permanent hardness is due to dissolved  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$



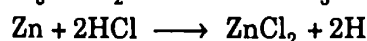
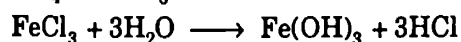
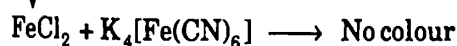
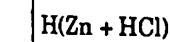
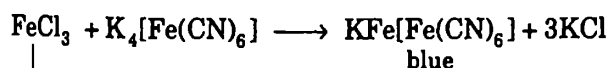
21. (d) 22. (c) 23. (a) 24. (d) 25. (d)

26. (d) 27. (c) 28. (c)



30. (a) 31. (d) 32. (a) 33. (d)

34. (b)  $\text{FeCl}_3$  solution is acidic due to hydrolysis when Zn is added, nascent hydrogen is formed which reduces  $\text{FeCl}_3$  to  $\text{FeCl}_2$  and thus no reaction with  $\text{K}_4[\text{Fe}(\text{CN})_6]$



$\text{H}_2$  gas is not effective in reducing  $\text{FeCl}_3$  to  $\text{FeCl}_2$

Thus, (b)

35. (b) 36. (c) 37. (d) 38. (d) 39. (d)

40. (b) 41. (c) 42. (a) 43. (b) 44. (a)

45. (d) 46. (a) 47. (c) 48. (d) 49. (c)

50. (a) 51. (b) 52. (a) 53. (c) 54. (a)

55. (b) 56. (c) 57. (c) 58. (b) 59. (d)

60. (a) 61. (b) 62. (b) 63. (c) 64. (b)

65. (d) 66. (a) 67. (d) 68. (d) 69. (c)

70. (d) 71. (c) 72. (d)

73. (b) Mass of one atom =  $6.66 \times 10^{-23}$  g

$$\begin{aligned} \text{Mass of } N_0 \text{ atoms} &= 6.66 \times 10^{-23} \times 6.02 \times 10^{23} \text{ g} \\ &= 40 \text{ g} \end{aligned}$$

Thus, atomic weight of the element = 40

| Element | %     | %/at wt. | Ratio |
|---------|-------|----------|-------|
| M       | 95.24 | 2.381    | 1     |
| H       | 4.76  | 4.76     | 2     |

Thus, hydride is  $\text{MH}_2$

Thus, (b)

74. (b) 75. (a) 76. (a) 77. (a)

78. (b)  $\text{Mg} + \text{H}_2\text{O} \xrightarrow{\Delta} \text{Mg}(\text{OH})_2 + \text{H}_2$ . other are for  $\text{H}_2\text{O}_2$

79. (c)

80. (a)  $\text{BaO}_2 + \text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{BaCO}_3 + \text{H}_2\text{O}_2$

81. (a) 82. (d) 83. (c) 84. (c) 85. (d)

86. (b) 87. (d) 88. (c) 89. (d)

90. (b) "20 volume" means

1 mL  $\text{H}_2\text{O}_2$  gives = 20 mL  $\text{O}_2$  at NTP

thus, 15 mL  $\text{H}_2\text{O}_2$  gives = 300 mL  $\text{O}_2$  at NTP

91. (b) 92. (b) 93. (d) 94. (c) 95. (c)

96. (d) 97. (d) 98. (b) 99. (c) 100. (d)

101. (b) 102. (b) 103. (d) 104. (b) 105. (c)

106. (d) 107. (d) 108. (b) 109. (c) 110. (d)

### One or More Than One Options Correct

1. (a, b, c, d) 2. (a) 3. (c) 4. (a, b, d) 5. (a, d)

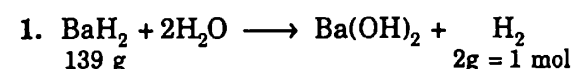
6. (c) 7. (a, b) 8. (a, b, c) 9. (a) 10. (a)

11. (d) 12. (b) 13. (d) 14. (a, b) 15. (a)

16. (a, b, c) 17. (a, b) 18. (a, b, c, d) 19. (b)

20. (a, d)

### Brain Twisters

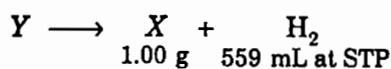
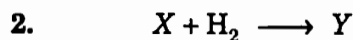


$$\begin{aligned} pV &= nRT \\ n &= \frac{pV}{RT} = \frac{0.975 \times 4.36}{0.0821 \times 293} \end{aligned}$$

$$= 0.1767 \text{ mol}$$

1 mol  $\text{H}_2$  is obtained from = 139 g  $\text{BaH}_2$

Hence, 0.1767 mol  $\text{H}_2$  is obtained from =  $139 \times 0.1767$   
 = 24.56 g  $\text{BaH}_2$



$$22400 \text{ mL } H_2 \text{ at STP} = 2 \text{ g } H_2$$

$$\therefore 559 \text{ mL } H_2 \text{ at STP} = \frac{2}{22400} \times 559 = 0.05 \text{ g } H_2$$

Also 559 mL  $H_2$  combines with = 1 g  $X$

$\therefore$  22400 mL  $H_2$  combines with = 40 g  $X$

Thus, atomic mass of  $X = 40 \text{ g mol}^{-1}$

Thus,  $X$  is Ca

Molecular formula of  $Y$

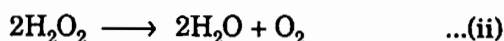
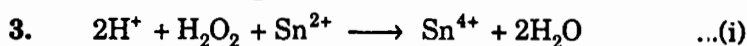
| Element | Amount | %      | Molar ratio | Simplest ratio |
|---------|--------|--------|-------------|----------------|
| Ca      | 1 g    | 95.24% | 2.38        | 1              |
| H       | 0.05 g | 4.76%  | 4.76        | 2              |

Thus,  $Y$  is  $CaH_2$

Molecular formula of  $Z$

| Element | %      | Molar ratio | Simplest ratio |
|---------|--------|-------------|----------------|
| Cl      | 63.89% | 1.80        | 2              |
| Ca      | 36.11% | 0.90        | 1              |

Thus,  $Z$  is  $CaCl_2$ .



$$200 \text{ g } H_2O_2 \text{ sample} = 200 \times \frac{10}{100}$$

$$= 20 \text{ g pure } H_2O_2$$

$$= 0.588 \text{ mol pure } H_2O_2$$

and  $100 \text{ mL of } 2M \text{ } Sn^{2+} = 0.2 \text{ mol } Sn^{2+}$

By reaction (i) :

$$0.2 \text{ mol } Sn^{2+} \text{ reduces} = 0.2 \text{ mol } H_2O_2$$

hence unreacted  $H_2O_2 = 0.588 - 0.200$   
 $= 0.388 \text{ mol}$

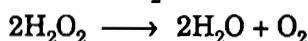
By reaction (ii) :

$$O_2 \text{ obtained from } 0.388 \text{ mol } H_2O_2 = \frac{0.388}{2} = 0.194 \text{ mol}$$

$$\therefore \text{Volume of } O_2 \text{ gas} = \frac{nRT}{p} = \frac{0.194 \times 0.0821 \times 293}{1}$$

$$= 4.67 \text{ L}$$

4.  $H_2O_2$  is marked "22.4 volume" which means 1 mL  $H_2O_2$  at NTP gives 22.4 mL of  $O_2$  at NTP.

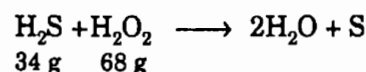


$$(2 \text{ mol} = 68 \text{ g}) \quad 22400 \text{ mL at NTP}$$

$$22400 \text{ mL of } O_2 \text{ is from} = 68 \text{ g } H_2O_2$$

$$22.4 \text{ mL of } O_2 \text{ is from} = \frac{68}{22400} \times 22.4 \text{ g } H_2O_2 = 0.068 \text{ g}$$

This amount is present in 1 mL  $H_2O_2$  solution.



$$34 \text{ g } H_2S \text{ is oxidised by} = 68 \text{ g } H_2O_2$$

$$3.4 \text{ g } H_2S \text{ is oxidised by} = \frac{68}{34} \times 3.4 = 6.8 \text{ g } H_2O_2$$

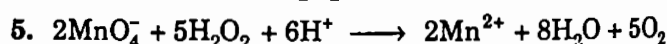
$$0.068 \text{ g } H_2O_2 \text{ is present in} = 1 \text{ mL}$$

$$\therefore 6.8 \text{ g } H_2O_2 \text{ is present in} = 100 \text{ mL}$$

Or density of "x volume"  $H_2O_2 = \frac{68x}{22400} \text{ g/mL}$

$$\text{density of "22.4 volume" } H_2O_2 = \frac{68 \times 22.4}{22400} = 0.068 \text{ g/mL}$$

$$\therefore 6.8 \text{ g } H_2O_2 \text{ is in} = 100 \text{ mL}$$



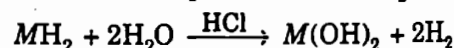
$$1000 \text{ mL of } 1N \text{ } MnO_4^- \equiv 1000 \text{ mL of } 1N \text{ } H_2O_2$$

Or equivalent of  $H_2O_2 = \text{equivalent of } MnO_4^-$   
 $= \frac{39.3 \times 0.5045}{1000} = 0.0198$

$$\therefore \text{Amount of pure } H_2O_2 = 0.0198 \times 17 = 0.337 \text{ g}$$

$$\% \text{ of } H_2O_2 \text{ in bleach solution} = \frac{0.337}{12.5} \times 100 = 2.69\%$$

6. Alkaline-earth metal hydride has  $M^{2+}$  (divalent cation) and  $H^-$ , hence, it can be represented as  $MH_2$ .



Number of moles of  $H_2$  collected

$$= \frac{pV}{RT} = \frac{\frac{750}{760} \times 1.0}{0.0821 \times 293}$$

$$= 0.041 \text{ mol}$$

$$\text{Thus, number of moles of } MH_2 = \frac{\text{moles of } H_2}{2} = \frac{0.041}{2}$$

$$= 0.0205 \text{ mol}$$

Let molar mass of  $M$  be =  $M$

then molar mass of  $MH_2 = (M + 2)$

$$\text{given number of moles } MH_2 = \frac{1.84}{M + 2}$$

$$\therefore \frac{1.84}{M + 2} = 0.0205$$

$$M + 2 = \frac{1.84}{0.0205} = 89.7$$

$$\therefore M = 87.7$$

Thus,  $M$  is Sr and hydride is  $SrH_2$ .

7.  $0.508 \text{ g } I_2 = \frac{0.508}{127} \text{ equivalent } I_2$   
 $= \frac{0.508}{127} \text{ equivalent } H_2O_2 \text{ in } 5 \text{ mL solution}$

$$\therefore N(H_2O_2) = \frac{0.508}{127} \times \frac{1000}{5} = 0.8 \text{ N}$$

$$\text{Volume strength} = N \times 5.6$$

$$= 0.8 \times 5.6$$

$$= 4.48 \text{ volume}$$





With Group 3 (boron family), we see the first evidence of a change from metallic behaviour of the elements at the left side of the Periodic Table to non-metal behaviour on the right side of the Table. Boron is a metalloid, whereas all the other elements of this group are metals.

# 11

## *p*-Block Elements —Boron Family (Group 13)

Shells up to  $(n-1)$  are completely filled and differentiating electron (last filling electron) enters into  $np$ -suborbitals — elements constitute what we call *p*-block elements.

| Group →<br>Period ↓ | 13<br>(IIIA) | 14<br>(IVA) | 15<br>(VA) | 16<br>(VIA) | 17<br>(VIIA) | 18<br>(VIIIA) |
|---------------------|--------------|-------------|------------|-------------|--------------|---------------|
| 2                   | B            | C           | N          | O           | F            | Ne            |
| 3                   | Al           | Si          | P          | S           | Cl           | Ar            |
| 4                   | Ga           | Ge          | As         | Se          | Br           | Kr            |
| 5                   | In           | Sn          | Sb         | Te          | I            | Xe            |
| 6                   | Tl           | Pb          | Bi         | Po          | At           | Rn            |
|                     | $ns^2np^1$   | $ns^2np^2$  | $ns^2np^3$ | $ns^2np^4$  | $ns^2np^5$   | $ns^2np^6$    |

- The *p*-block elements are characterised by the  $ns^2np^x$  valence shell electronic configuration where  $x$  varies from 1 to 6 and  $n$  from 2 to 6 but inner core for different elements may be different.
- The highest oxidation state = (group number – 10)  
Stability of this oxidation state (OS) decreases and that of  $[(OS) - 2]$  state increases as we move down the group—a case of **inert pair effect**. This is shown below in Table 11.1
- Trends in properties of *p*-block elements have been represented in Fig. 11.1

### Learning Framework of the Chapter

- Group 13(IIIA) (The Boron Family)
- Compounds of Boron
- Compounds of Aluminium



Table 11.1 Common Oxidation States of *p*-Block Elements

| Group           | 13                   | 14                   | 15                  | 16                          | 17                              | 18                   |
|-----------------|----------------------|----------------------|---------------------|-----------------------------|---------------------------------|----------------------|
| Oxidation state | B<br>+3              | C<br>+4, -4          | N<br>+5 to -3       | O<br>-1, -2                 | F<br>-1                         |                      |
|                 | Al<br>+3             | Si<br>+4             | P, As<br>+3, +5, -3 | S, Se, Te<br>-2, +2, +4, +6 | Cl, Br, I<br>-1, +1, +3, +5, +7 | Xe<br>+2, +4, +6, +8 |
|                 | Ga, In, Tl<br>+3, +1 | Ge, Sn, Pb<br>+4, +2 | Sb, Bi<br>+3, +5    |                             |                                 |                      |

## The van Arkel-Ketelaar Triangle

Before looking at the compounds of the *p*-block elements in detail, it will be useful to consider the general types of compound we will expect and this, as we shall see, can often be rationalized on the basis of electronegativities,  $\chi$ , and electronegativity differences,  $\Delta\chi$ . Thus, compounds with a large  $\Delta\chi$  will tend to be ionic and those with medium  $\Delta\chi$  are likely to form polar covalent bonds and therefore, have polymeric or macromolecular structures. For compounds with a small  $\Delta\chi$ , the type of compound will depend on whether the elements have a low or high electronegativity. In the former case, the compounds are likely to be metallic for much the same reason that elements with low electronegativity are metals. In the latter case, we shall expect relatively non-polar molecular species.

### DEEP Focus

A useful way to visualize these ideas is with the so called van Arkel-Ketelaar or element triangle, shown in Fig. 11.2 in which the vertices are labelled metallic, covalent and ionic in such a way that the vertical and horizontal axes represent electronegativity, difference,  $\Delta\chi$ , and absolute electronegativity,  $\Sigma\chi$ , respectively and are defined such that, for a molecule *AB*,  $\Delta\chi = \chi_B - \chi_A$  and  $\Sigma\chi = (\chi_A + \chi_B)/2$ .

The metallic-covalent edge of the van Arkel-Ketelaar triangle comprises the elements themselves, since  $\Delta\chi$  is zero, and ranges from metals on the left to covalent species such as  $F_2$  on the right.

The ionic-covalent edge is characterized by decreasing  $\Delta\chi$  which is well illustrated with the fluorides of the elements. Thus,  $CsF$  and  $LiF$  are ionic with large  $\Delta\chi$  whereas  $NF_3$  and  $CF_4$  both have small  $\Delta\chi$  and are covalent; compounds with intermediate  $\Delta\chi$  such as  $BeF_2$  are polymeric or macromolecular solids.

|                            |    |    |    |    |    |                                                      |    |
|----------------------------|----|----|----|----|----|------------------------------------------------------|----|
| $p, q, r$                  |    |    |    |    |    | $p, z$<br>$q, r, s$<br>(except for $N_2, O_2, F_2$ ) |    |
| $x, y, t$                  | B  | C  | N  | O  | F  |                                                      | Ne |
|                            | Al | Si | P  | S  | Cl |                                                      | Ar |
|                            | Ga | Ge | As | Se | Br |                                                      | Kr |
|                            | In | Sn | Sb | Te | I  | Xe                                                   |    |
|                            | Tl | Pb | Bi | Po | At | Rn                                                   |    |
| $x, y, z$ (up to group 14) |    |    |    |    |    |                                                      |    |

where ... represents

$x$ : covalent/van der Waals' radius

$y$ : metallic character

$z$ : heat of sublimation

$p$ : electronegativity

$q$ : ionisation energy ( $N > O, P > S$ )

$r$ : oxidising power

$s$ : stability of higher oxidation state within a group

$t$ : stability of lower oxidation state within a group

Fig. 11.1 Trends in properties of *p*-Block elements in the direction of arrow

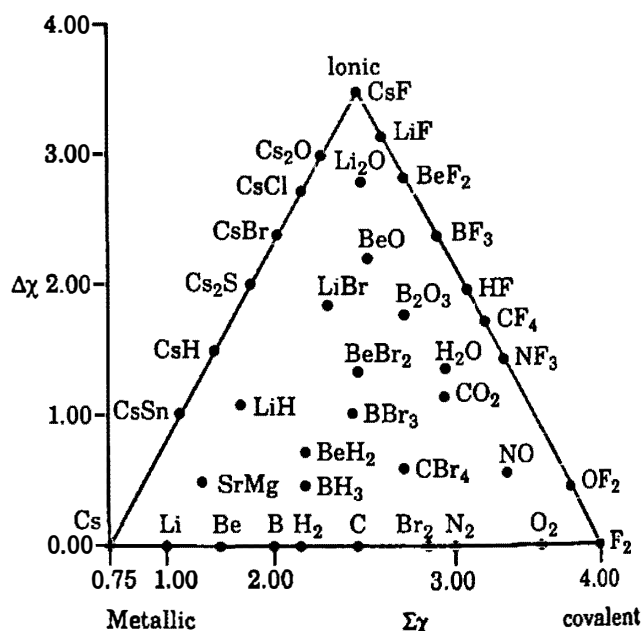


Fig. 11.2 A van Arkel-Ketelaar triangle showing the position of selected compounds and elements

## Group 13 (IIIA) (The Boron Family)

This group marks the beginning of the *p*-block elements. Table 11.2 summarises the properties of this group, and trends shown in Fig. 11.3.

### DEEP Focus

Elements of group 13 are less metallic than those of groups 1 and 2. Within the group, there is a variation in metallic character. Boron, the smallest element in this group is a non-metal. The other elements in this group are fairly reactive metals.

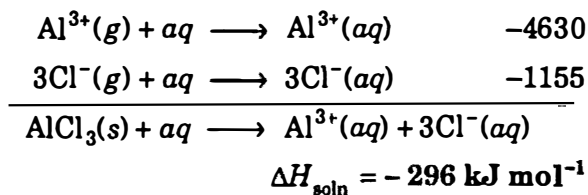
The elements of group 13 have smaller atomic radii and higher electronegativities as compared to s-block elements of the same period. Since, the size and the ionisation energies of atoms depend on effective nuclear charge of the atom, insertion of transition elements result in higher effective nuclear charge of the fourth row elements Ga, Ge, etc., than expected by simple extrapolation from the second and third row elements. In other words, **the nuclei of these fourth row elements attract electrons more strongly than expected and this affects their properties. Thus, the atomic size of gallium is smaller; its electronegativity and ionisation energies higher than expected.** Atoms with  $d^{10}$  inner shell, in general, are smaller and have higher ionisation energies. In a similar way, the inclusion of fourteen electrons in 4f-orbital further affects the size and ionisation energy of Tl. As a result of this, irregularities in atomic radii, electronegativity and ionisation energies are seen from B to Tl.

Table 11.2 shows that densities of these elements show a gradual increase while melting and boiling points fall in value. **The exceptionally low melting point of gallium (303 K), however, has, so far, no simple explanation.**

From Table 11.2 we observe that these elements form small ions of high charge density and the value of the sum of their first, second and third ionisation energies is very high. These properties lead us to the conclusion that these elements will prefer to form covalent rather than ionic compounds. **Boron is always covalent and does not form  $B^{3+}$  ions, because the energy required to remove three electrons is very high.** Many simple compounds of Al and Ga like  $AlCl_3$  and  $GaCl_3$  are also covalent when anhydrous. However, in solution, the large amount of hydration energy evolved compensates the high ionisation energy and all the metal ions exist in a hydrated state.

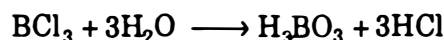
This can be explained with the help of **Born-Haber cycle** as given below.

|                                                         | $\Delta H$ (kJ) |
|---------------------------------------------------------|-----------------|
| $AlCl_3(s) \longrightarrow Al(s) + \frac{3}{2} Cl_2(g)$ | 704             |
| $Al(s) \longrightarrow Al(g)$                           | 326             |
| $\frac{3}{2} Cl_2(g) \longrightarrow 3Cl(g)$            | 366             |
| $Al(g) \longrightarrow Al^{3+}(g) + 3e^{-}$             | 5137            |
| $3Cl(g) + 3e^{-} \longrightarrow 3Cl^{-}(g)$            | -1044           |



#### Born-Haber cycle for formation of $Al^{3+}(aq)$ ion

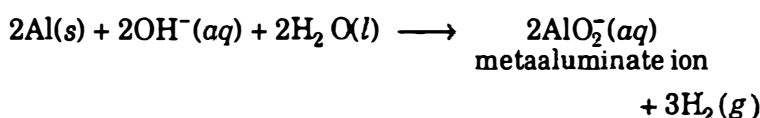
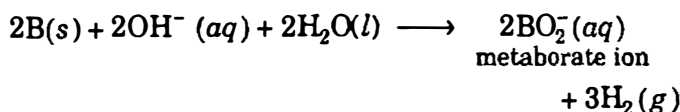
Thus, despite the large ionisation energies of aluminium, the enthalpy of solution of  $AlCl_3$  has a large negative value. Therefore, in aqueous solution,  $AlCl_3$  exists as  $Al^{3+}(aq)$  and  $Cl^{-}(aq)$ .  $BCl_3$  hydrolyses in aqueous solution to give boric acid and not  $B^{3+}(aq)$



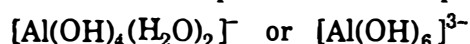
This group is the most metallic in nature of the p-block elements and only boron is non-metallic.

**Boron and aluminium show an oxidation state of +3 in their compounds while gallium, indium and thallium also show +1 oxidation state (due to inert pair effect).**

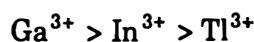
- Both boron and aluminium are amphoteric.



but the ions are better represented as complex ions.

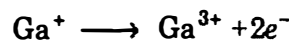


- B and Al show +3 oxidation state. Ga, In and Tl show +3 and +1 oxidation state but stability order is

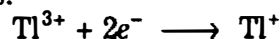


due to **inert-pair effect**.

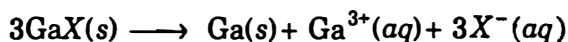
Thus,  $Ga^{+}$  salts tend to stabilise by changing to  $Ga^{3+}$  ( $Ga^{3+} > Ga^{+}$ ) and thus are better reducing agents.



On the other hand,  $Tl^{3+}$  salts tend to stabilise by changing to  $Tl^{+}$  ( $Tl^{+} > Tl^{3+}$ ) and thus are better oxidising agents.



$GaX$ ,  $InX$  and  $TlX$  ( $X = Cl, Br, I$ ) exist.  $GaX$  and  $InX$  disproportionate in water



All the above reaction are spontaneous and  $\Delta G^{\circ} < 0$

Table 11.2 Physical Properties of the Elements of Group 13 (IIIA)

| Property                                   | B                | Al               | Ga                       | In              | Tl              |
|--------------------------------------------|------------------|------------------|--------------------------|-----------------|-----------------|
| Electronic structure                       | [He] $2s^2 2p^1$ | [Ne] $3s^2 3p^1$ | [Ar] $3d^{10} 4s^2 4p^1$ | ... $5s^2 5p^1$ | ... $6s^2 6p^1$ |
| Electronegativity (Pauling)                | 2.0              | 1.5              | 1.6                      | 1.7             | 1.8             |
| $(IE)_1$ kJ mol <sup>-1</sup>              | 801              | 577              | 579                      | 558             | 589             |
| $(IE)_2$ kJ mol <sup>-1</sup>              | 2427             | 1816             | 1979                     | 1820            | 1971            |
| $(IE)_3$ kJ mol <sup>-1</sup>              | 3659             | 2744             | 2962                     | 2704            | 2877            |
| m.p./°C                                    | 2180             | 660              | 30                       | 157             | 303             |
| b.p./°C                                    | 3650             | 2467             | 2403                     | 2080            | 1457            |
| Density ( $10^3 \times \text{kg m}^{-3}$ ) | 2.34             | 2.7              | 5.91                     | 7.3             | 11.8            |
| Metallic radius/pm                         | 88.5             | 143              | 141                      | 166             | 170             |
| Ionic radius/pm $M^{3+}$                   | 27.0             | 53.5             | 62                       | 80              | 88.5            |
| $M^+$                                      | —                | —                | 120                      | 140             | 150             |
| Principal coordination number              | 3, 4             | 3, 4, 6          | 3, 6                     | 3, 6            | 3, 6            |
| $E^\circ_{M^{3+}/M}$ / V *                 | —                | -1.66            | -0.56                    | -0.38           | +2.18           |
| $E^\circ_{M^+/M}$ / V                      | —                | 0.55             | —                        | -0.18           | -0.34           |

\* For Al and Ga in acidic solutions, others in basic solution.

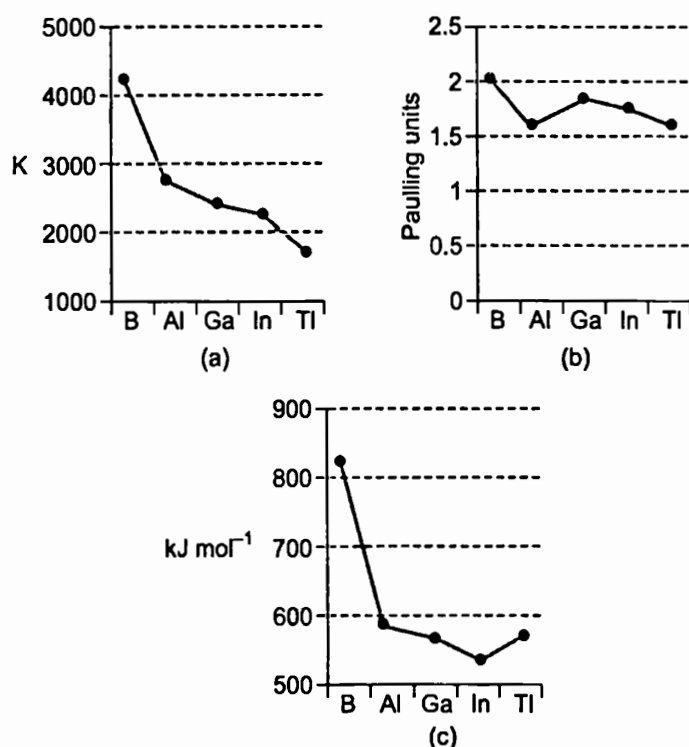


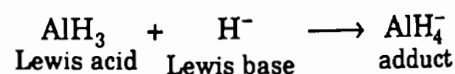
Fig. 11.3 Some group trends of the group 13 elements : (a) Boiling point, (b) Pauling electronegativity, and (c) The first ionisation energy.

The term 'inert pair effect' is somewhat misleading. The decrease stability of the higher oxidation state (+3) with increasing atomic number arises because of the decrease in bond energy with size from Al to Tl. As a result, the energy required to unpair  $ns^2$  electrons is not compensated by the energy released in forming the two additional bonds.

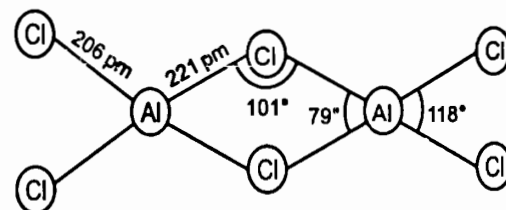
- Except boron, the other elements of group 13 (IIIA) show increasing metallic character from Al to Tl. Small size (atomic radius = 88.5 pm) and relatively

high nuclear charge provide boron with non-metallic properties.

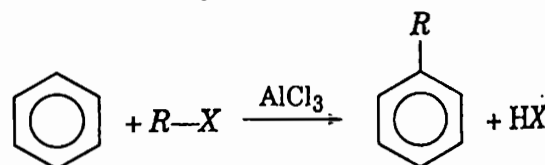
- Except boron, other exist in aqueous solution in tripositive ( $M^{3+}$ ) state.  $[M(H_2O)_6]^{3+}$ ,  $[M(H_2O)_2(OH)_4]^-$  and  $[M(OH)_4]^-$  exist in aqueous solution.
- Stability of hydrides ( $MH_3$ ) decreases as we move down the group.  $AlH_3$  is a solid and is polymerised via Al—H—Al bridging units. Hydrides are electron-deficient and thus act as Lewis acids (lone pair acceptor) and form adducts with strong Lewis bases.



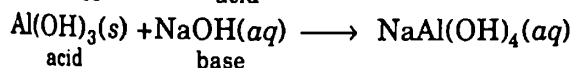
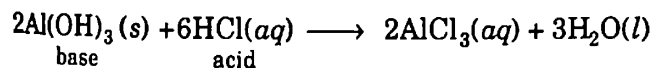
- They form halides of the type  $MX_3$ , all of which are known except Tl(III) iodide.
  - fluorides are ionic with high melting point
  - chlorides, bromides and iodides are covalent with low melting point
  - halides have halogen bridged dimeric structures as shown.



- $MX_3$  are strong Lewis acids. Anhydrous  $AlCl_3$  is used as a catalyst in Friedel-Craft's reaction



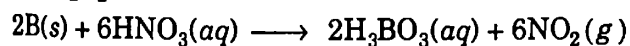
- They form oxides and hydroxides of the type  $M_2O_3$  and  $M(OH)_3$  and their basic nature increases as we move down the group. **However,  $Al_2O_3$  and  $Ga_2O_3$  (and their hydroxides) show amphoteric nature.**



- They form octahedral aqua complexes of the type  $[M(H_2O)_6]^{3+}$  ( $M = Al, Ga, In, Tl$ )
- Aluminium sulphate forms double salt with alkali sulphates of the type  $MAI(SO_4)_2 \cdot 12H_2O$  ( $M^+ = Na^+$  or  $K^+$ ). These are called **alums**.
- $(IE)_1$  of boron is relatively high and  $(IE)_2$  and  $(IE)_3$  are still higher. Thus, the total energy required to give  $B^{3+}$  ions is far more than that which would be compensated by lattice energies of ionic compounds or hydration of such ions in solution. As a result, boron does not easily form a cation; however their covalent compounds are known.
- The melting point of B is very high which suggests a strong bonding between individual atoms in solid state and is used as a **semi-conductor**.

## Reactions of Elements

Pure crystalline boron is very unreactive. However, it is attacked at high temperatures by strong oxidising agents such as a mixture of hot concentrated  $H_2SO_4$  and  $HNO_3$  or  $Na_2O_2$ .

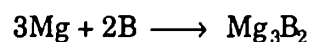


In contrast, finely divided amorphous boron (containing about 2–5% impurities) is more reactive. Reactions are summarised in Table 11.3.

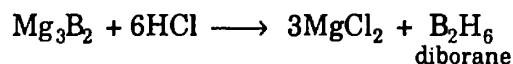
Table 11.3 Reactions of Group 13 (IIIA) Elements

| Reaction                                            | Comment                                                                                                                                             |
|-----------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------|
| $4M + 3O_2 \longrightarrow 2M_2O_3$                 | Reaction at high temperature; with Al—exothermic, a protective oxide layer is formed and Tl also forms $Tl_2O$ .                                    |
| $2M + N_2 \longrightarrow 2MN$                      | Only Al and (B) form nitrides. BN, a slippery white solid with layer structure similar to graphite.                                                 |
| $2M + 3X_2 \longrightarrow 2MX_3$                   | All form $MX_3$ . Tl also form $TlX$ . Iodide of $Tl^{3+}$ ( $TlI_3$ ) is not formed; but $TlI$ reacts with $I_2$ forming $TlI_3$ ( $Tl^+ I_3^-$ ). |
| $2M + 2NaOH + 2H_2O \longrightarrow 2NaMO_2 + 3H_2$ | B, Al and Ga only form $NaMO_2$ .                                                                                                                   |
| $2M + 6NH_3 \longrightarrow 2M(NH_2)_3 + 3H_2$      | All form amides except B which forms BN.                                                                                                            |
| $2B + 2NH_3 \longrightarrow 2BN + 3H_2$             |                                                                                                                                                     |
| $2M + 6H^+ \longrightarrow 2M^{3+} + 3H_2$          | Metals liberate $H_2$ , but $HNO_3$ makes Al passive.                                                                                               |

- Boron reacts directly with elements forming borides which are hard and refractory.

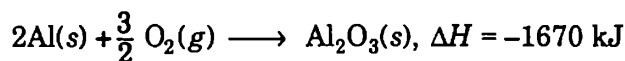


Borides are decomposed by acids forming boranes.

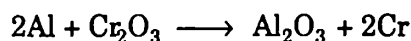
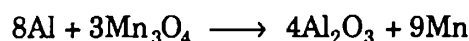


## DEEP Focus

- Aluminium is far more reactive than boron but in air and water it is stable. It is due to the formation of aluminium oxide,  $Al_2O_3$  layer, that makes it passive for further attack.  $HNO_3$  also makes Al passive by oxide layer formation. The layer is so useful that in industry it is purposely increased by an electrolytic process called **anodising**. This is done by electrolysis of dilute  $H_2SO_4$  with Al as anode. This produces much thicker layer of oxide on the surface (0.01 mm). *This layer can take up pigments; thus colouring the aluminium.*
- Reaction of Al with  $O_2$  is exothermic and is called **thermite reaction**.

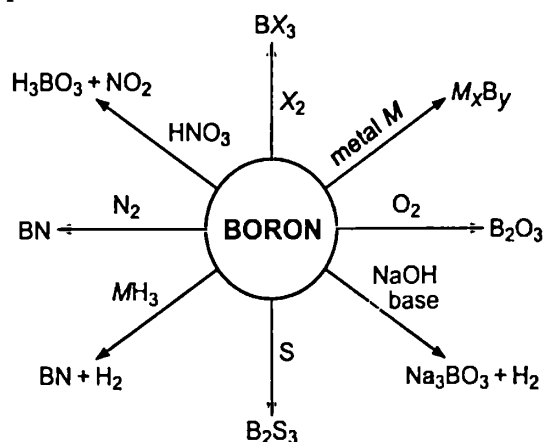


*The thermite reaction involves so much energy that it can be dangerous. The Al becomes white hot and often causes fires. For this precise reason, mixture of Al and an oxide such as  $Fe_2O_3$  or  $SiO_2$  (a source of oxygen) were used to make incendiary bombs during World War II. Warships are sometimes made of aluminium alloys to reduce their weight. A thermite reaction can be started if the ship is hit by a missile. Thermite reaction also finds applications in the metallurgical extraction of other metals from their oxides :*



In recent years, Al has been under suspicion as a possible cause of **Alzheimer's** disease. This disease induces senility in relatively young men and women. The disease causes them to lose their memory.

- Most of the reactions of boron are at high temperatures.



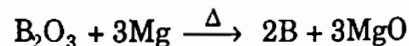
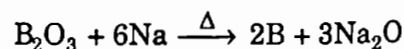
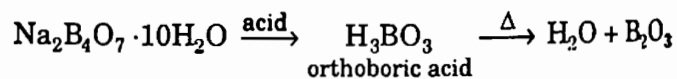
## Differences between Boron and the other Elements

Boron because of its small size has high ionisation energy and electronegativity. It is always covalent and non-metallic. It differs other elements of its group in the following respects :

| Boron                                                                                         | Other elements                                       |
|-----------------------------------------------------------------------------------------------|------------------------------------------------------|
| • $B_2O_3$ is an acidic oxide (like $SiO_2$ )                                                 | • $Al_2O_3$ is amphoteric                            |
| • $H_3BO_3$ is acidic                                                                         | • $Al(OH)_3$ is amphoteric                           |
| • Simple borate and silicate ions can polymerise forming isopolyacids by sharing oxygen atoms | • Aluminates are formed but do not polymerise        |
| • Boranes are gaseous compounds readily hydrolysed and spontaneously inflammable              | • Aluminium hydride $(AlH_3)_n$ is a polymeric solid |
| • Halides are easily hydrolysed                                                               | • Halides are easily hydrolysed                      |

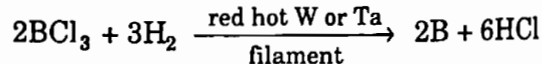
## Boron : Extraction

Amorphous boron (called Moissan boron) is obtained by reduction of  $B_2O_3$  with Na or Mg at a high temperature.  $B_2O_3$  in turn is obtained by decomposing borax with acid and subsequent heating.

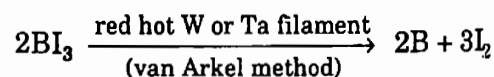


Boron obtained is 95–98% pure and black in colour. Pure crystalline boron is obtained by

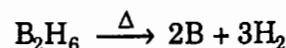
- reducing  $BCl_3$  with  $H_2$ :



- pyrolysis of  $BI_3$

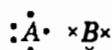


- thermal decomposition of  $B_2H_6$



## Target Practice 1

- A and B with valence electrons are represented below



What can be possible formula of the compound of A and B?

- Write structure of  $Al_2Cl_6$ .

- Do as directed

(a) Increasing order of stability of  $M^{3+}$  of Group 13 in 4th, 5th and 6th period.

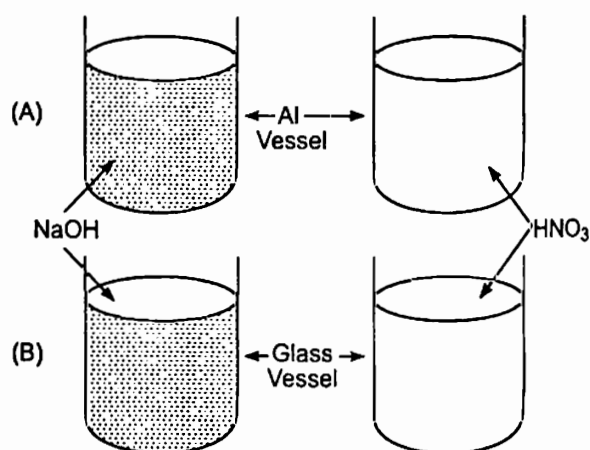
(b) Hydrolysis reaction of  $BCl_3$ .

(c) Intermediates formed when  $AlCl_3$  reacts with  $CH_3Cl$ .

(d) Non-metal of group 13

(e)  $TiCl_3$  is unstable because

- NaOH and  $HNO_3$  are being manufactured in industries A and B and stored as shown



Comment .....

- Disease due to Al metal is .....

This disease causes .....

- Write the nature of the following

(a)  $B_2O_3$  .....

(b)  $Al_2O_3$  .....

(c)  $Al(OH)_3$  .....

(d)  $B(OH)_3$  .....

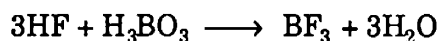
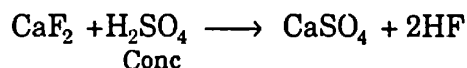
10. In an ordinary fire the reactions are kept going by the material reacting with oxygen in the air. Water not only cools the fire, but also keeps oxygen out. In the thermite reaction, the oxygen involved is in the metal oxide, so keeping atmospheric oxygen out has no effect. Also high temperature (about  $1000^{\circ}\text{C}$ ) will allow reaction between Al and  $\text{H}_2\text{O}$  to give off  $\text{H}_2$ .

## Compounds of Boron

Boron is the first member of group 13 (IIIA) of the Periodic Table and is the only non-metal of this group, having three valence electrons. Because of its small size, high ionisation energy and low electronegativity, boron forms covalent compounds and in this respect resembles carbon and silicon. Since, compounds formed are electron-deficient, they behave as Lewis acids (electron-pair acceptors)

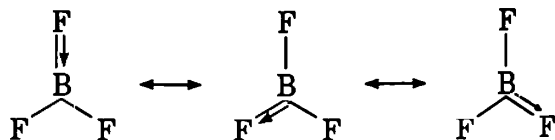
### Boron Halides

- Boron halides are covalent. It is due to the extremely small size of  $B^{3+}$  ion (27 pm) and can polarise the anion easily (smaller the size of cation, larger the size of anion, greater the charge  $\Rightarrow$  greater the polarising power hence, greater the covalent nature —Fajan's rule)
  - $BF_3$  is a gas
  - $BCl_3$  is a liquid
  - $BI_3$  is a solid
- When borates are treated with HF (or  $CaF_2$  and concentrated  $H_2SO_4$ ), the volatile compound  $BF_3$  is formed. If the  $BF_3$  gas produced is introduced into a bunsen flame, a characteristic green colouration is formed :

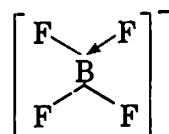
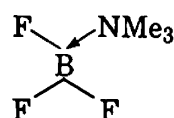
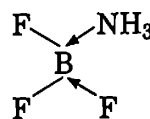
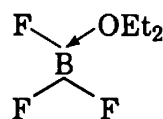


**This can be used to test borates.**

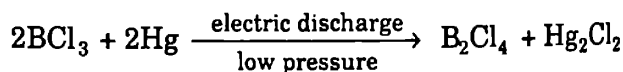
- $BX_3$  is electron-deficient (octet of B incomplete) and thus behaves as a Lewis acid. The shape of the  $BF_3$  molecule is a planar triangle with bond angles of  $120^\circ$ .
- The bond lengths in  $BF_3$  are  $1.30\text{\AA}$  and are shorter than the sum of the covalent radii ( $B = 0.80\text{\AA}$  and  $F = 0.72\text{\AA}$ ). The bond energy is very high ( $646\text{ kJ mol}^{-1}$ ) and is higher than for any single bond. The shortness and strength of (B—X) bond is interpreted in terms of a  $p\pi-p\pi$  interaction. The empty  $2p_z$  atomic orbital on B (which is not involved in hybridisation) is perpendicular to the triangle containing the  $sp^2$  hybrid orbitals. This  $2p_z$  orbital may accept an electron pair from a full  $p_z$  orbital on any one of the three fluorine atoms. Thus a dative bond is formed and the B atom attains an octet of electrons. If one localised double bond existed, there would be one short bond and two longer ones. **But all B—F bonds are equivalent and based on modern explanation, the double bond is delocalised.**



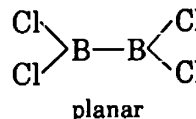
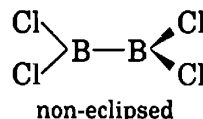
- The empty  $2p_z$  orbitals on the boron atom in  $BF_3$  can also be filled by a lone pair of electrons from donor molecules such as ether ( $Et_2O$ ),  $NH_3$ ,  $(Me)_3N$  or  $F^-$  and tetrahedral molecule or ion is formed.



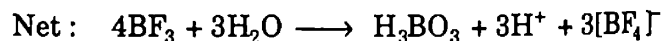
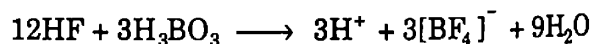
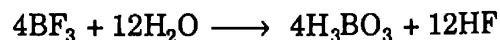
- Boron also forms halides of the formula  $B_2X_4$ . These decompose slowly at room temperature.  $B_2Cl_4$  can be made as follows :



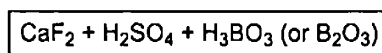
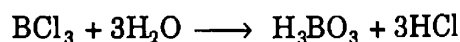
There is free rotation about the B—B bond, and in the gaseous and liquid states the molecule adopts a non-eclipsed conformation. In the solid state the molecule is planar, because of crystal forces and ease of packing.



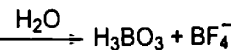
- $BF_3$  hydrolyses incompletely and forms fluoroborates. This is because the HF first formed reacts with the  $H_3BO_3$  :



The other halides hydrolyse completely, giving boric acid.



$\Delta$



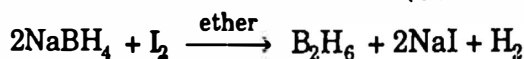
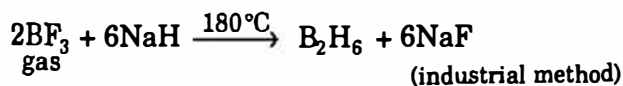
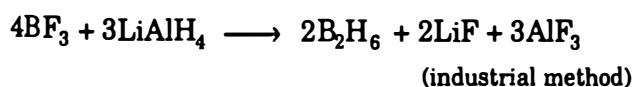
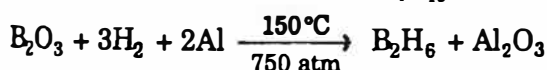
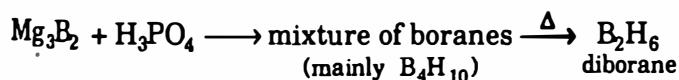
$180^\circ\text{C}$  NaH



## Boron Hydrides

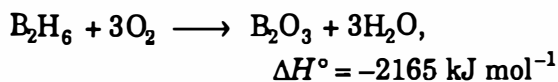
- The boron hydrides are sometimes called **boranes** by analogy with the alkanes (hydrocarbons).
- There are two series :
  - $B_nH_{n+4}$  called **nido-boranes**, ( $B_2H_6$ )
  - $B_nH_{n+6}$  called **arachno-boranes**, (less stable), ( $B_4H_{10}$ );
  - of all these, diborane is the simplest borane.

## Source

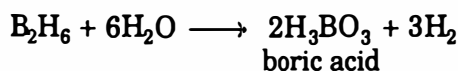


## Properties

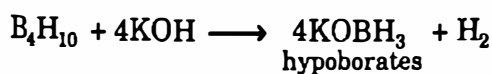
- Diborane is a colourless gas, highly reactive (b.p. 180 K). It catches fire spontaneously in air and explodes with oxygen :



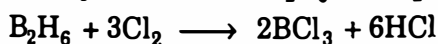
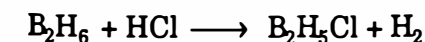
- It is hydrolysed by water :



- In alkaline solution, hypoborates are formed.

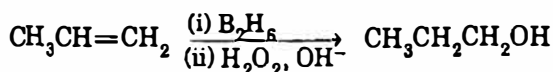


Both  $LiBH_4$  and  $NaBH_4$  are used as reducing agents in organic synthesis.

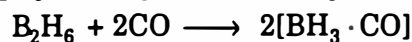
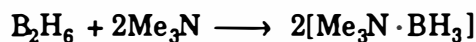


## DEEP Focus

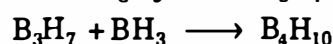
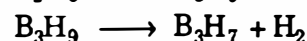
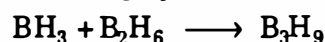
- $B_2H_6$  selectively changes alkenes to alcohol with alkaline  $H_2O_2$  against Markownikoff's rule :



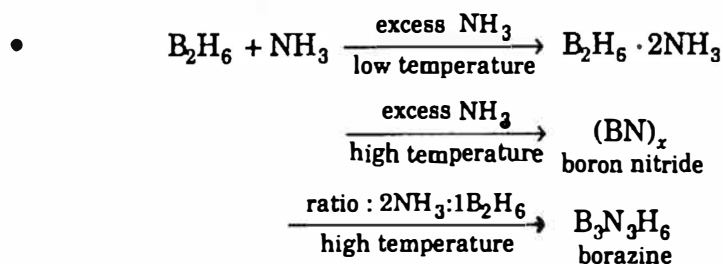
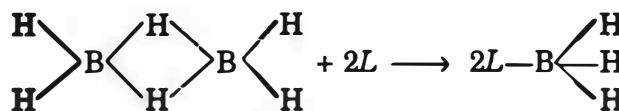
- All the boranes act as Lewis acids and can accept electron pairs. Thus they react with amines, forming simple adducts. They also react with ammonia to give variety of products depending on experimental conditions:



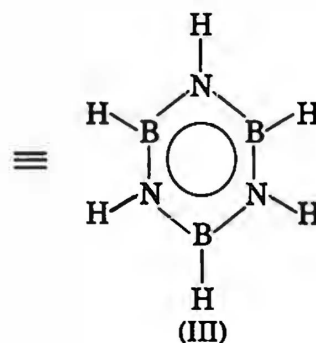
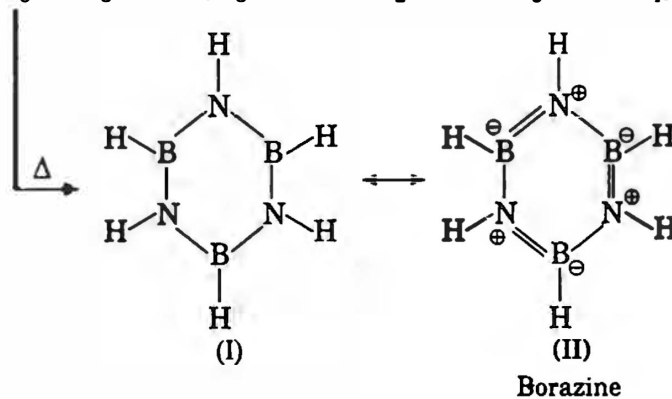
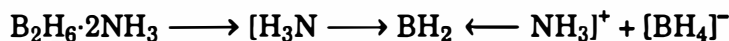
A complex reaction occurs when  $B_2H_6$  is heated in a sealed tubes. The  $B_2H_6$  molecule probably breaks into the reactive intermediate  $BH_3$  which combines with  $B_2H_6$  forming another intermediate  $B_3H_9$  which can now further reactions :



$B_2H_6$  splits into two symmetrical fragments ( $BH_3$ ) in presence of Lewis acid ( $L$ ) to give borane-adducts  $BH_3 \cdot L$ . This is called **symmetric or homolytic cleavage**.



$B_2H_6 \cdot 2NH_3$  is ionic and **forms borazine on heating** :

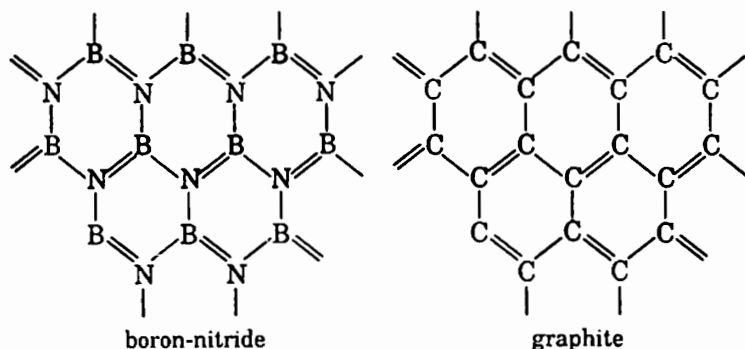




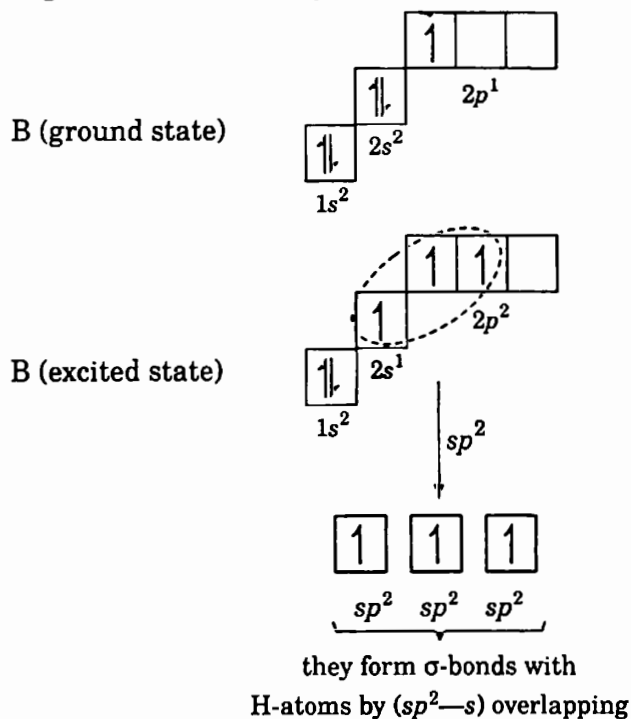
**DEEP Focus**

Borazine,  $B_3N_3H_6$  (I) is called 'inorganic benzene' because its structure shows some formal similarity with benzene, with delocalised electrons (II) and aromatic character (III).

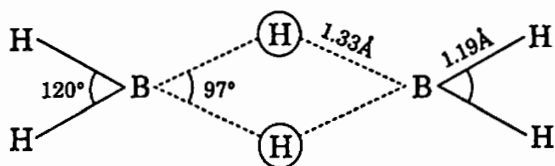
- Boron nitride is a white slippery solid. One B atom and one N atom together have the same number of valence electrons as two C atoms. Thus boron nitride has almost the same structure as graphite, with sheets made up of hexagonal rings of alternate B and N atoms joined together (inorganic graphite).



- In borane, boron atom is  $sp^2$  hybridised with bond angle of  $120^\circ$  and having triangular planar structure.

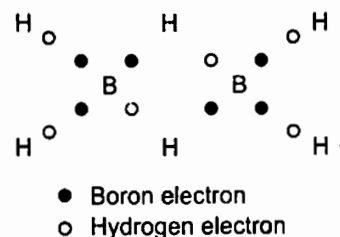


- The molecular shapes of diborane is shown below :

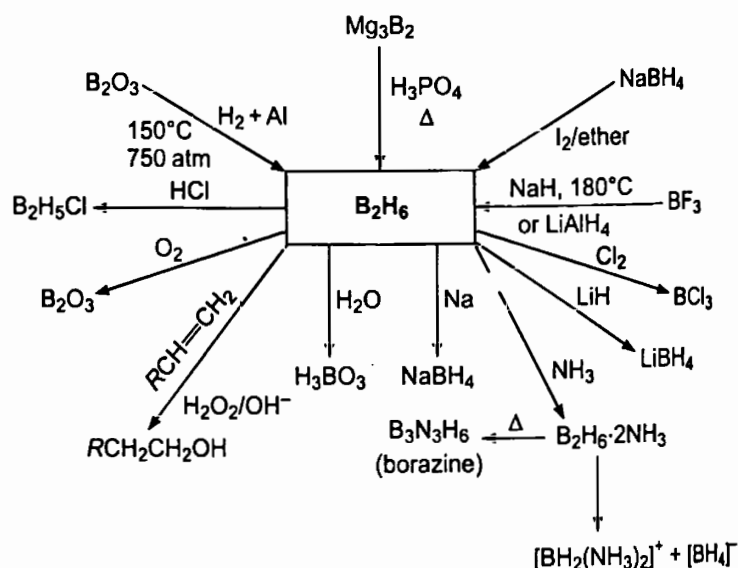
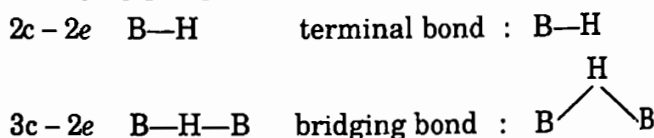
**DEEP Focus**

The two boron atoms and the four terminal hydrogen atoms lie in one plane; the two bridging hydrogen atoms (encircled) lie symmetrically above and below the plane. There are total 12 valence electrons—6 in two B and 6 in six H atoms and they form in all eight B—H bonds. Evidently, there are not

enough electrons to fill all the available orbitals to form eight normal—two-centre two-electron ( $2c-2e$ ) or electron pair bonds. The two bridging hydrogen atoms lie symmetrically above and below this plane ( $3c-2e$  bonding). This has actually multicentre bonds or odd-electron bonds and B—H bond lengths (of terminal sides) is less than that of central B—H bonds.

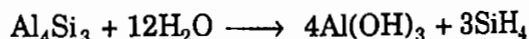
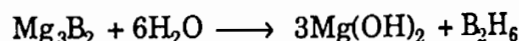


(Bridging groups are electron deficient).

**Similarity between Boron and Silicon (Diagonal Relationship)**

- Both form volatile hydrides (called boranes and silanes) which spontaneously catch fire on exposure to air and are easily hydrolysed.
- Halides of both (except  $BF_3$ ) are easily hydrolysed :
 
$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$

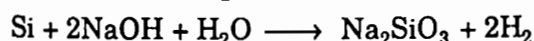
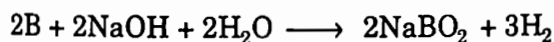
$$SiCl_4 + 4H_2O \longrightarrow H_4SiO_4 + 4HCl$$
- Boron forms binary compounds with several metals—these are called borides. Silicon forms silicides. Borides and silicides are hydrolysed by  $H_2O$  forming boranes and silanes :



- $B_2O_3$  and  $SiO_2$  are acidic in nature and are important constituents of glass. Borate and silicates have

tetrahedral  $\text{BO}_4$  and  $\text{SiO}_4$  structural units, respectively.

- Both are semi-conductors.
- Boric acid ( $\text{H}_3\text{BO}_3$ ) and silicic acids ( $\text{H}_4\text{SiO}_4$ ) are weak acids.
- Both exist in two allotropic forms—amorphous and crystalline.
- They do not dissolve in cold dilute acids but do so in alkalies—boron only in fused alkalies and silicon in both fused and aqueous alkalies.

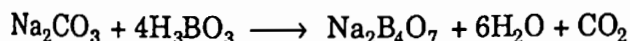


### Borax : ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ )

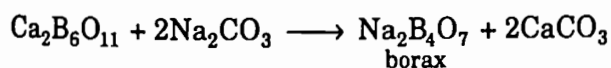
#### Source

- Tincal (*suhaga*) occurs naturally and contains about 45% borax. Tincal is dissolved in water and after removing impurities (by filtration), aqueous solution is evaporated to get crystals of borax.

- Orthoboric acid,  $\text{H}_3\text{BO}_3$  on neutralisation with  $\text{Na}_2\text{CO}_3$  gives borax.

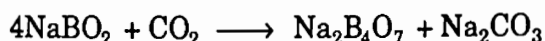


- Colemanite,  $\text{Ca}_2\text{B}_6\text{O}_{11}$  is converted into borax by boiling it with concentrated solution of  $\text{Na}_2\text{CO}_3$ .



+2NaBO<sub>2</sub>  
sodium metaborate  
(in mother liquor)

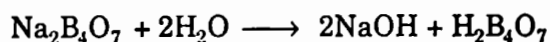
$\text{CO}_2$  is passed into mother liquor containing  $\text{NaBO}_2$  when borax is formed.



#### Properties

- Borax is
  - prismatic,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  obtained by crystallising salt at ordinary temperature.
  - octahedral,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$  obtained by crystallising salt above 370 K. It is also called **jeweller's borax**.
  - borax glass,  $\text{Na}_2\text{B}_4\text{O}_7$ , obtained by heating ordinary borax above its melting point. It is colourless glassy substance which absorbs moisture from air and is converted into  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ .

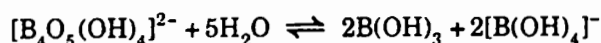
- Borax dissolves in water to give alkaline solutions :



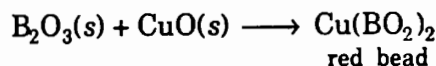
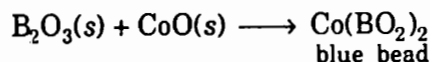
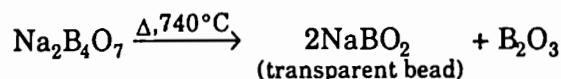
Borax is therefore, used as a water softener and cleansing agent.

#### DEEP Focus

- One mole of borax reacts with two moles of  $\text{HCl}$  (or one mole  $\text{H}_2\text{SO}_4$ ). This is because when borax is dissolved in water both  $\text{B(OH)}_3$  and  $[\text{B(OH)}_4]^-$  are formed, but only the  $[\text{B(OH)}_4]^-$  reacts with  $\text{HCl}$ . Each  $[\text{B(OH)}_4]^-$  has one neutralisable  $\text{OH}^-$  ion.

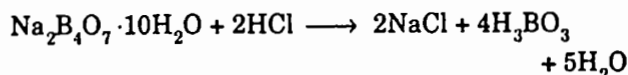


- Borax on strongly heating forms  $\text{B}_2\text{O}_3$  which form coloured glassy bead with coloured oxide (generally of transition metals). It is called **borax bead test**.



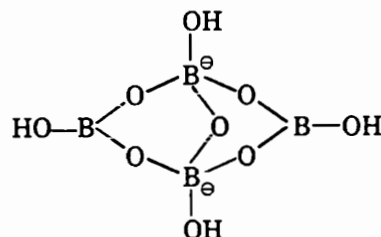
#### DEEP Focus

- Borax is used as a primary standard in titrations against acids.

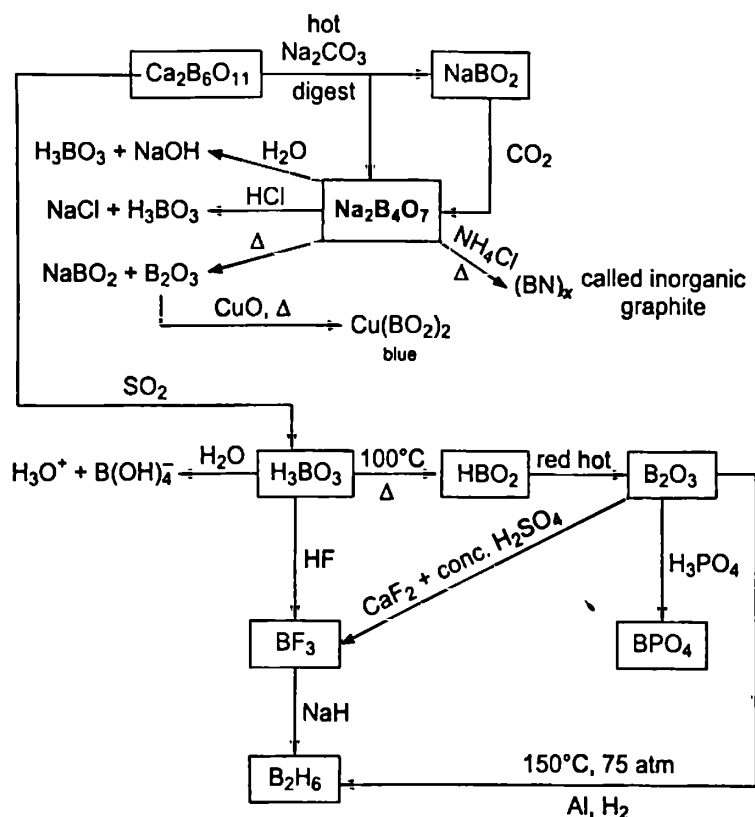


One of the products  $\text{H}_3\text{BO}_3$  is itself a weak acid. Thus, the indicator used to detect end point of this reaction must be one that is unaffected by  $\text{H}_3\text{BO}_3$ . **Methyl orange (pH range 3.1–4.4) is normally used.**

- Borax is actually made of two tetrahedra and two triangular units joined as shown and should be written as  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ .



- It is used as a flux in welding and brazing metals for dissolving any oxide which may form on the surfaces to be joined; in the manufacture of high quality heat resistant glass (borosil-mark) Jena and pyrex glasses contain boric oxide.



## Boric acids and oxides

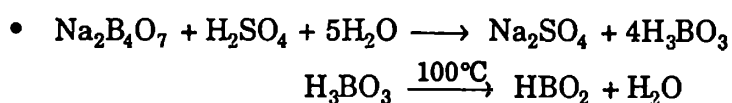
(i)  $\text{H}_3\text{BO}_3$  or  $\text{B}(\text{OH})_3$  orthoboric acid.

(ii)  $\text{HBO}_2$  or  $\text{BO}(\text{OH})$  metaboric acid.

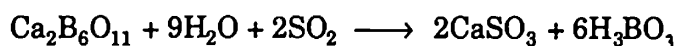
(iii)  $\text{H}_2\text{B}_4\text{O}_7$  pyroboric acid

Boric acid is the trivial name for ortho boric acid. In aqueous solution *meta* and pyroboric acid are changed into *ortho* boric acid.

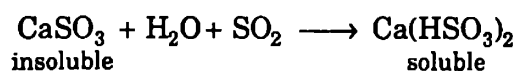
## Source



- On a commercial scale, boric acid is prepared from colemanite,  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ . Mineral (colemanite) is powdered finely and  $\text{SO}_2$  is passed into hot aqueous suspension. On cooling crystals of boric acid are obtained.

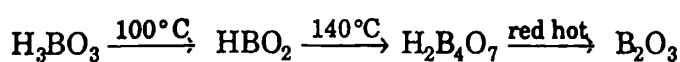


Excess of  $\text{SO}_2$  dissolves  $\text{CaSO}_3$  as  $\text{Ca}(\text{HSO}_3)_2$



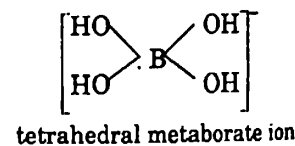
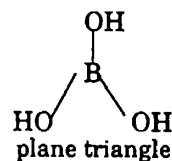
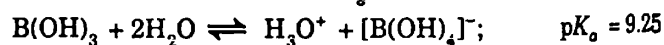
## Properties

- Both form  $\text{B}_2\text{O}_3$  (boron sesquioxide — sesqui means one and a half, so the oxide should have  $\text{BO}_{1\frac{1}{2}}$  or  $\text{B}_2\text{O}_3$ )

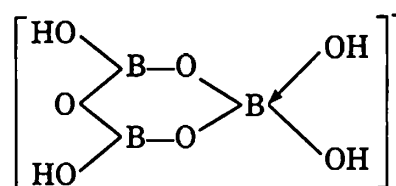
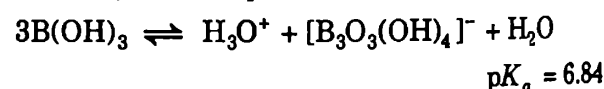


## DEEP Focus

- Ortho boric acid,  $\text{H}_3\text{BO}_3$  is soluble in water and behaves as a weak monobasic acid. It does not donate protons like most acids, but rather it accepts  $\text{OH}^-$ . It is therefore a Lewis acid, and is better written as  $\text{B}(\text{OH})_3$ .



- Polymeric metaborate species are formed at higher concentration, for example :



- Orthoboric acid contains triangular  $\text{BO}_3^{3-}$  units. In the solid the  $\text{B}(\text{OH})_3$  units are hydrogen bonded together into two-dimensional sheets with almost hexagonal symmetry (Fig. 11.4). The layers are quite a larger distance apart ( $3.18\text{\AA}$ ) and thus the crystal breaks quite easily into very fine particles.

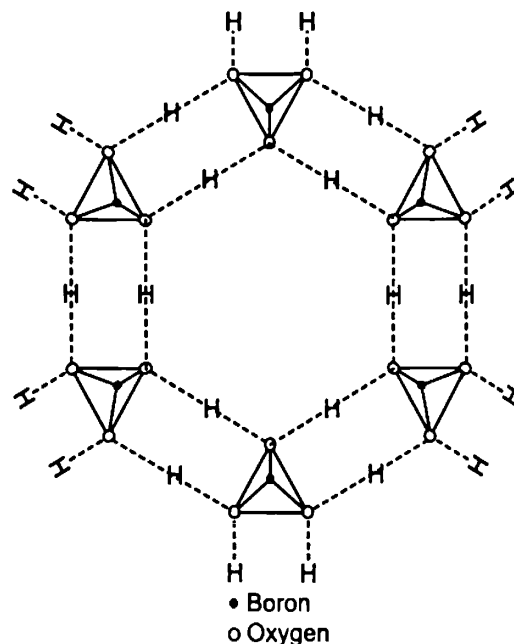


Fig.11.4 Hydrogen bonded structure of orthoboric acid

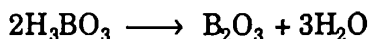
- It is used in the manufacture of enamels and glazes for pottery and as disinfectant in medicine.

## Boron trioxide ( $\text{B}_2\text{O}_3$ )

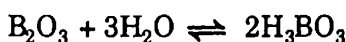
- This ( $\text{B}_2\text{O}_3$ ) is obtained when boron is burnt in oxygen



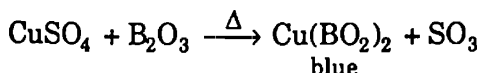
- It is also obtained as a colourless glass when boric acid is heated to redness



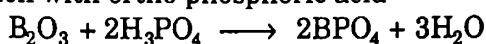
- $\text{B}_2\text{O}_3$  is a white non-volatile glassy solid.
- It is an acidic oxide giving rise to boric acid, when dissolved in water



- Boron trioxide reacts with various metallic salts at high temperatures giving characteristic coloured beads. This is called **borax-bead test** of the identification of coloured salts



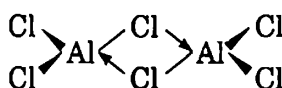
- $\text{B}_2\text{O}_3$  also shows weakly basic properties as indicated by its reaction with ortho phosphoric acid



## Compounds of Aluminium

### Aluminium Halides

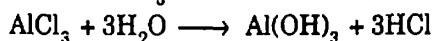
$\text{AlX}_3$  ( $X = \text{Cl}, \text{Br}$ ) exists as dimer, thus attaining an octet of electrons. The dimer formula is retained when the halides dissolve in non-polar solvents (like ether, benzene).



### DEEP Focus

However, when the halides dissolve in  $\text{H}_2\text{O}$ , the high enthalpy of hydration is sufficient to break the covalent dimer into  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$  and  $3\text{X}^-$  ions.

Aqueous solution of  $\text{AlCl}_3$  is acidic due to hydrolysis



$\text{AlCl}_3$ , being electron deficient, finds use as Lewis acid catalyst in Friedel-Craft's reactions of aromatic class.

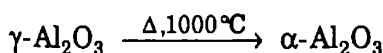
### Aluminium Oxide and Hydroxide

#### Source

- Alumina,  $\text{Al}_2\text{O}_3$  can be made by dehydrating  $\text{Al}(\text{OH})_3$ , or from elements.  $\text{Al}_2\text{O}_3$  is

$\alpha\text{-Al}_2\text{O}_3$  or corundum

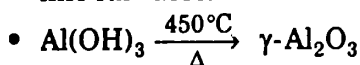
$\gamma\text{-Al}_2\text{O}_3$



#### Properties

- Corundum is extremely hard and is used as 'jewellers rouge' to polish glass. Its impure form containing  $\text{Fe}_2\text{O}_3$  and silica is called **emery** and is used to make emery paper (sand paper) used to polish metals. It is

also unaffected by acids and is used as refractory to line furnaces.

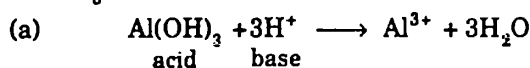


$\gamma\text{-Al}_2\text{O}_3$  dissolves in acids, absorbs moisture and is used in chromatography.

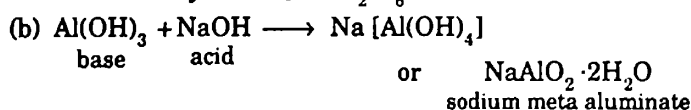
- Alumina is white in colour and addition of  $\text{Cr}_2\text{O}_3$  or  $\text{Fe}_2\text{O}_3$  makes it coloured.

### DEEP Focus

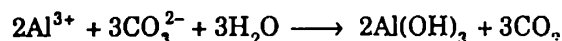
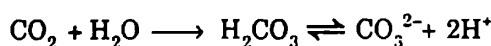
- $\text{Al}(\text{OH})_3$  is amphoteric.



$\text{Al}^{3+}$  exists as hydrated  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  ion.



In (a) it behaves as a base while in (b) it behaves as an acid—thus amphoteric. However,  $\text{Al}^{3+}$  is precipitated as  $\text{Al}(\text{OH})_3$  on passing  $\text{CO}_2$ , showing that the acidic properties are very weak.

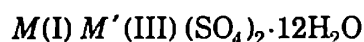


- Structure of aluminate ion changes with both pH and concentration :

- between pH 8 and 12, the ions polymerise using OH bridges and each Al is octahedrally coordinated.
- in dilute solution above pH 13, a tetrahedral  $\text{Al}(\text{OH})_4^-$  exists.
- in concentrated solutions above 1.5 M and pH greater than 13, it exists as a dimer  $[(\text{OH})_3\text{Al}-\text{O}-\text{Al}(\text{OH})_3]^{2-}$ .

### Alums

An aqueous solution containing equimolar amounts of  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{K}_2\text{SO}_4$  crystallises as potassium aluminium sulphate,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . This is generally called **alums** with general formula



where  $\text{M(I)}$  is almost any unipositive cation [except  $\text{Li}^+$ , because this ion is too small to meet the structural requirements of the crystal] and  $\text{M' (III)}$  is a tripositive cation— $\text{Al}^{3+}, \text{Ti}^{3+}, \text{V}^{3+}, \text{Cr}^{3+}, \text{Fe}^{3+}, \text{Mn}^{3+}, \text{Co}^{3+}, \text{Ga}^{3+}, \text{In}^{3+}, \text{Re}^{3+}, \text{Ir}^{3+}$ ]. Alums contain the ions  $[\text{M}(\text{H}_2\text{O})_6]^+$ ,  $[\text{M'}(\text{H}_2\text{O})_6]^{3+}$  and  $\text{SO}_4^{2-}$  in the ratio 1 : 1 : 2. Most common alums have  $\text{M(I)} = \text{K}^+$  or  $\text{NH}_4^+$  and  $\text{M' (III)} = \text{Al}^{3+}$ .

Alums are used as mordant in dyeing. The fabric to be dyed is dipped in a solution of the alum and heated with steam. Hydrolysis of  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  deposits  $\text{Al}(\text{OH})_3$  into the fibres of the material and the dye is adsorbed on the  $\text{Al}(\text{OH})_3$ .

## Cement

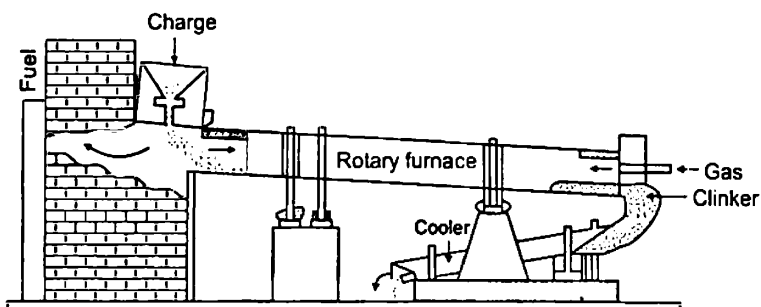
- $\text{Ca}_3\text{Al}_2\text{O}_6$  (tricalcium aluminate) is important constituent of Portland and high alumina cements.
- General formula is  $\text{Ca}_9[\text{Al}_6\text{O}_{18}]$  because it contains 12-membered rings of  $\text{Si}-\text{O}-\text{Si}-\text{O}$  made by joining six  $\text{AlO}_4$  tetrahedra.
- Portland cement is made by heating mixture of  $\text{CaCO}_3$ ,  $\text{SiO}_2$  and clay (aluminosilicate) at a temperature of  $1450 - 1600^\circ\text{C}$  in a rotary kiln. When mixed with sand and water, Portland cement sets to give a concrete, a hard whitish solid (with appearance similar to Portland cement). About 2-5% of gypsum [ $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ] is added to slow down the setting process to increase strength.

Portland cement has:

|                         |     |                                           |    |
|-------------------------|-----|-------------------------------------------|----|
| $\text{CaO}$            | 70% | $\text{Fe}_2\text{O}_3$                   | 3% |
| $\text{SiO}_2$          | 20% | $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ | 2% |
| $\text{Al}_2\text{O}_3$ | 5%  |                                           |    |

- High alumina cement is made by fusing limestone and bauxite with small amount of  $\text{SiO}_2$  and  $\text{TiO}_2$  at  $1400-1500^\circ\text{C}$ . It is better than Portland cement in terms of:

- it sets much quicker,
- it develops high strength within one day,
- it has good resistance to sea water and dilute mineral acids.



|                         |     |                         |     |
|-------------------------|-----|-------------------------|-----|
| It has                  |     |                         |     |
| $\text{CaO}$            | 40% | $\text{SiO}_2$          | 10% |
| $\text{Al}_2\text{O}_3$ | 40% | $\text{Fe}_2\text{O}_3$ | 10% |

### DEEP Focus

- When mixed with water, the setting of cement takes place. Chemically, it is hydration of the molecules of constituents and their rearrangement. The adhesion of other particles to each other and to the embedded aggregates is responsible for the strength of the cement which is due, ultimately, to the formation of  $\text{Si}-\text{O}-\text{Si}-\text{O}$  bonds.

## Uses

Boron is used to increase the hardness of steels. Crystalline boron is used in transistors. Boron is a good neutron absorber and is used as shields and control rods in **nuclear reactors**. Boranes are used as **high energy fuels**, for example, in rockets. **Boric acid is used as an antiseptic**. Borax is used to make **heat resistant borosilicate glass**. It is also used for **vitreous enamelling** of baths, domestic appliances and for glazing

tiles and pottery. Another use of borax is to make peroxyborates, e.g.,  $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ , which are **useful cleaning and bleaching agents**. In the laboratory, borax is used for standardising acids and in the borax bead test in qualitative analysis.

Aluminium exhibits useful properties of low density, high thermal and electrical conductivity, good corrosion resistance with non-toxic nature of the metal and its compounds. Due to these properties, it is the most widely used non-ferrous metal. Aluminium is used for making electrical conductors, cooking utensils and wrapping materials. Aluminium is extensively used for structural purposes, either alone or alloyed, in aircraft, ship and building industries. Large amounts of aluminium are converted into alloys, such as, duralumin and magnalium containing a few per cent of copper or magnesium. These alloys are harder and stronger than pure aluminium but possess almost the same properties of lightness and corrosion resistance which can be further increased by anodising process. Aluminium beryllium alloys are harder and lighter than other alloys of aluminium and are extensively used in space-craft. However, toxic nature of beryllium makes their handling difficult. Due to its strong affinity for oxygen, aluminium is a good reducing agent and is used in aluminothermic process for extraction of metals and in welding. Suspension of finely powdered aluminium in oil is used as paint.

Anhydrous  $\text{AlCl}_3$  is an important catalyst, used in organic synthesis and in the cracking of petroleum.  $\text{Al}_2(\text{SO}_4)_3$  as such or as potash alum,  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  is used for sizing paper, for tanning leather, for waterproofing cloth and as a mordant for dyeing cotton. It is extensively used for purification of water and in sewage treatment.

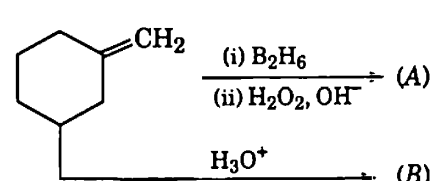
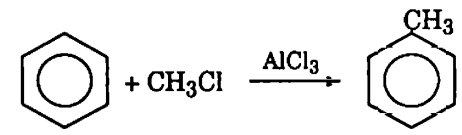
Because of its extreme hardness, high melting point, non-volatility, chemical inertness and good electrical insulating properties, **corundum ( $\text{Al}_2\text{O}_3$ ) finds many applications in abrasives, refractories and ceramics**. Large crystals of  $\alpha\text{-Al}_2\text{O}_3$  when coloured with metal-ion impurities are prized as gemstones, e.g., ruby ( $\text{Cr}^{3+}$ , red), sapphire ( $\text{Fe}^{2+/3+}\text{Ti}^{4+}$ , blue), oriental emerald ( $\text{Cr}^{3+}/\text{V}^{3+}$ , green), oriental topaz ( $\text{Fe}^{3+}$ , yellow), etc. Aluminates are important constituents of Portland cement. Gallium has the longest liquid range ( $303-2343\text{ K}$ ) of any known substance and so finds use as a high temperature thermometer liquid.

### Some Gemstones Based on $\text{Al}_2\text{O}_3$

| Gem             | Impurity |
|-----------------|----------|
| White sapphire  | none     |
| Blue sapphire   | Fe, Ti   |
| Green sapphire  | Co       |
| Yellow sapphire | Ni, Mg   |
| Star sapphire   | Ti       |
| Ruby            | Cr       |

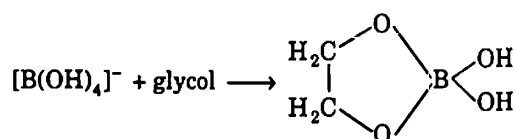
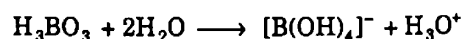


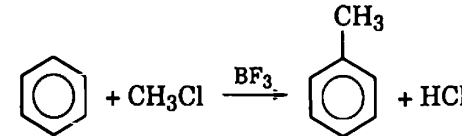
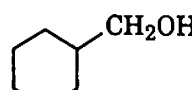
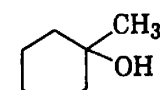
## Practice Exercise 2

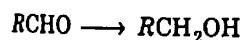
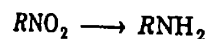
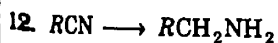
- The end-point of a borax–acid titration is at about pH = 4. What indicator would you use in the titration?
- $\text{Na}_2\text{B}_4\text{O}_7 + \text{conc. H}_2\text{SO}_4 \longrightarrow (\text{A}) \xrightarrow[\text{(ii) ignite}]{\text{(i) C}_2\text{H}_5\text{OH}} (\text{B})$   
(B) is identified by the characteristic colour of the flame. Identify (A) and (B).
- You should know that the oxides of non-metals are acidic and the oxides of the metals are basic. Would you expect boron to be more acidic or more basic than aluminium in its reactions?
- Identify (A), (B) and (C).  
$$\text{Na}_2\text{B}_4\text{O}_7 + \text{NaOH} \longrightarrow (\text{A}) \xrightarrow{\text{HCl}} (\text{B}) \xrightarrow{\text{H}_2\text{O}} (\text{C})$$
- Borates are identified by “Flame Test”. Give the chemistry of this test.
- What happens when glycol reacts with orthoboric acid?
- $\text{B}_2\text{O}_3$  is an acidic oxide. Give examples.
- Identify (A), (B) and (C).  
$$\begin{aligned} \text{Na}_2\text{B}_4\text{O}_7 &\xrightarrow{\Delta} (\text{A}) + (\text{B}) \\ (\text{A}) + \text{NaOH} &\longrightarrow (\text{B}) \\ (\text{A}) + \text{HF} &\xrightarrow{\text{H}_2\text{SO}_4} (\text{C}) \end{aligned}$$
- $\text{BCl}_3$  or  $\text{BI}_3$  can be converted into pure B. Write chemical reactions.
- $\text{BF}_3$  finds use as Lewis acid catalyst in Friedel-Crafts reaction. Give example.
- Identify (A), and (B) in the following:  

- $\text{RCN}$ ,  $\text{RNO}_2$  and  $\text{RCHO}$  can be reduced by  $\text{B}_2\text{H}_6$ . What are the products due to reduction?
-   
What is the function of  $\text{AlCl}_3$  in this reaction? Also name the reaction.
- Aluminium salts turn blue litmus red. Explain.
- A mixture contains  $\text{ZnO}$  and  $\text{Al}_2\text{O}_3$ . Give a scheme to separate them.

## Answers

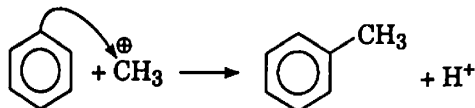
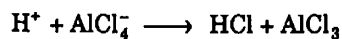
- Methyl orange.
- (A) :  $\text{H}_3\text{BO}_3$  (B) :  $\text{B}(\text{OC}_2\text{H}_5)_3$  : gives green-edged flame.
- Being nearer the top of the group, we would expect boron to show more non-metallic nature than aluminium; so it should be more acidic in nature than aluminium.
- (A) :  $\text{NaBO}_2$  (B) :  $\text{HBO}_2$  (C) :  $\text{H}_3\text{BO}_3$   
$$\text{Na}_2\text{B}_4\text{O}_7 + 2\text{NaOH} \longrightarrow 4\text{NaBO}_2 + \text{H}_2\text{O} \quad (\text{A})$$
$$\text{NaBO}_2 + \text{HCl} \longrightarrow \text{HBO}_2 + \text{NaCl} \quad (\text{B})$$
$$\text{HBO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{BO}_3 \text{ or } \text{B}(\text{OH})_3 \quad (\text{C})$$
- $\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_2\text{SO}_4 \xrightarrow{\Delta} \text{Na}_2\text{SO}_4 + 4\text{H}_3\text{BO}_3 + 5\text{H}_2\text{O}$   
borax  
$$\text{H}_3\text{BO}_3 + 3\text{C}_2\text{H}_5\text{OH} \xrightarrow{\Delta} \text{B}(\text{OC}_2\text{H}_5)_3 + 3\text{H}_2\text{O}$$
  
triethyl borate  
Triethyl borate burns with green-edged flame when ignited.
- Cis*-di-ol form very stable complex with  $[\text{B}(\text{OH})_4]^-$  which is formed when  $\text{H}_3\text{BO}_3$  reacts with  $\text{H}_2\text{O}$  :



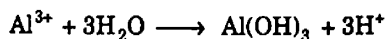
- $\text{B}_2\text{O}_3 + 6\text{HCl} \longrightarrow 2\text{BCl}_3 + 3\text{H}_2\text{O}$   
 $\text{B}_2\text{O}_3 + 2\text{NaOH} \longrightarrow 2\text{NaBO}_2 + \text{H}_2\text{O}$
- (A) :  $\text{B}_2\text{O}_3$  (B) :  $\text{NaBO}_2$  (C) :  $\text{BF}_3$
- $2\text{BCl}_3 + 3\text{H}_2 \xrightarrow{\text{red hot W}} 2\text{B} + 6\text{HCl}$   
 $2\text{BI}_3 \xrightarrow{\text{red hot W}} 2\text{B} + 3\text{I}_2$
- 
- (A) :  (B) : 



13. It is Friedel-Craft's reaction.  $\text{AlCl}_3$  acts as Lewis acid that helps in the formation of carbocation ion (in this case  $\text{CH}_3^+$  without which  $S_E$  (Electrophilic substitution) reaction is not possible:

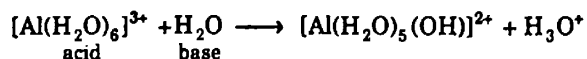


14. Aluminium salts are acidic due to hydrolysis of  $\text{Al}^{3+}$



Aluminum salts also exist as  $[\text{Al(H}_2\text{O)}_6]^{3+}$ .

In the following reaction it behaves like an acid ( $\text{H}^+$  ion donor)

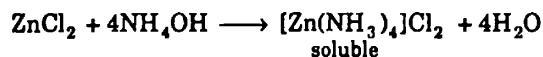
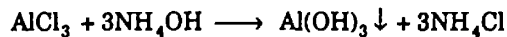


15.  $\text{ZnO}$  and  $\text{Al}_2\text{O}_3$  both are amphoteric. They can be separated by:

*Step I* : Dissolve in dil.  $\text{HCl}$  when  $\text{ZnCl}_2$  and  $\text{AlCl}_3$  are formed.

*Step II* : Add  $\text{NH}_4\text{Cl}$  and then  $\text{NH}_4\text{OH}$  dropwise.

$\text{Al}^{3+}$  is precipitated as  $\text{Al(OH)}_3$  and  $\text{Zn}^{2+}$  is soluble.

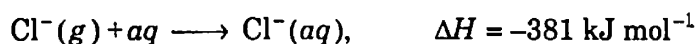
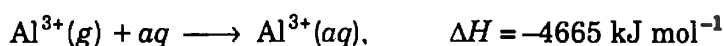
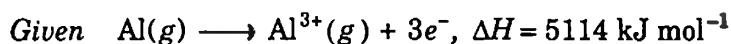




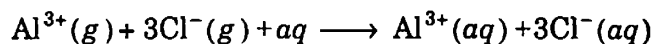
# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** Whereas  $\text{AlCl}_3$  is always covalent, it ionises in solution inspite of high ionisation energy. Explain.



**Solution**  $\text{Al}^{3+}$  will be formed from  $\text{AlCl}_3$  in solution if heat of hydration of  $\text{AlCl}_3$  is greater than total ionisation energy of  $\text{Al}(g)$ .



$\Delta H = -4665 + 3(-381) = -5808 \text{ kJ mol}^{-1}$



$\Delta H = 5114 \text{ kJ mol}^{-1}$

Thus,  $\Delta H(\text{hydration}) > \Delta H(\text{ionisation})$

Thus,  $\text{AlCl}_3$  ionises in solution.

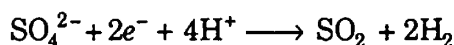
**Problem 2.**  $E^\circ_{\text{Al}^{3+}/\text{Al}} = -1.66 \text{ V}$ ;  $E^\circ_{\text{SO}_4^{2-}/\text{SO}_2} = 1.17 \text{ V}$ .

What, if anything, would happen if you reacted aluminium with sulphuric acid? If you think a reaction would take place, write down the equation.

**Solution** The given reaction (say dissolution of Al into  $\text{H}_2\text{SO}_4$ ) is possible if  $E^\circ_{\text{cell}}$  is positive.

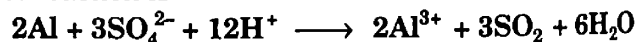


$E^\circ_{\text{Al}/\text{Al}^{3+}} = -E^\circ_{\text{Al}^{3+}/\text{Al}} = 1.66 \text{ V}$



$E^\circ_{\text{SO}_4^{2-}/\text{SO}_2} = 1.17 \text{ V}.$

Net reaction is



Thus,  $E^\circ_{\text{cell}}$  is 2.83 V hence Al can reduce  $\text{SO}_4^{2-}$  to  $\text{SO}_2$ .

**Problem 3.** The standard free energies of formation of  $\text{B}_2\text{O}_3$  and  $\text{MgO}$  are  $-1194 \text{ kJ mol}^{-1}$  and  $-569 \text{ kJ mol}^{-1}$  respectively. Should it be possible to prepare boron by reacting  $\text{B}_2\text{O}_3$  with magnesium.



$\Delta G^\circ = \Delta G^\circ_{\text{product}} - \Delta G^\circ_{\text{reactant}}$

$= 3\Delta G^\circ_f(\text{MgO}) - \Delta G^\circ_f(\text{B}_2\text{O}_3)$

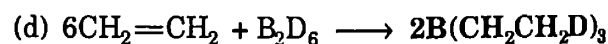
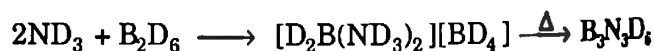
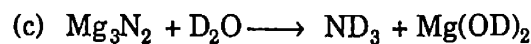
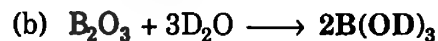
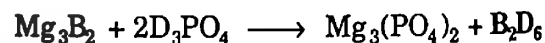
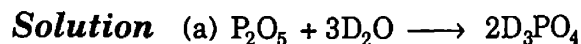
$= 3(-569) - (-1194)$

$= -513 \text{ kJ mol}^{-1} \quad [\Delta G^\circ_f(\text{element}) = 0]$

The negative sign of  $\Delta G^\circ$  shows that the reaction should be spontaneous. (However, the reaction is initially endothermic when two reactants are heated.)

**Problem 4.** Suggest synthesis (starting from deuterium oxide as the only source of deuterium) for:

(a)  $\text{B}_2\text{D}_6$  (b)  $\text{B}(\text{OD})_3$  (c)  $\text{B}_3\text{N}_3\text{D}_6$  (d)  $\text{B}(\text{CH}_2\text{CH}_2\text{D})_3$



## Explanation

(a) **Boron does not usually form a cation :**

B has

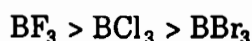
$$(IE)_1 = 801 \text{ kJ mol}^{-1}, (IE)_2 = 2427 \text{ kJ mol}^{-1},$$

$$(IE)_3 = 3659 \text{ kJ mol}^{-1}$$

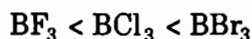
- Thus, the total energy required to give  $B^{3+}$  ions is far more than that which would be compensated by lattice energies of ionic compounds or hydration of such ions in solution. Thus formation of cation (like  $B^{3+}$ ) is not possible.

(b) **The polarity of B—X bonds is in the order : B—F > B—Cl > B—Br but Lewis acidity shows the sequence :  $BF_3 < BCl_3 < BBr_3$ .**

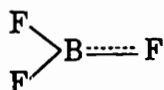
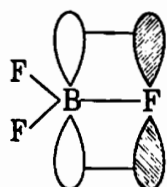
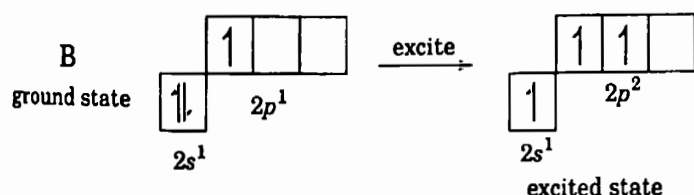
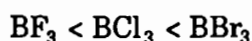
- With increase in polarity of B—X bond, acidity also increases and should be thus in the order :



But Lewis acidity is in reverse order :

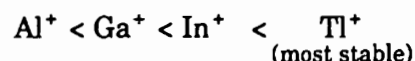
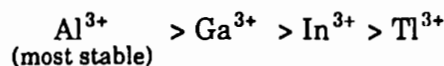


There is lateral overlap of the vacant  $2p$ -orbital of B with one completely filled orbital of F leading to  $p\pi-p\pi$  bonds between B and F. This B—F bond thus acquires double bond character. This also leads to compensate electron deficiency of boron and thus Lewis acid character of  $BF_3$  is reduced. This  $p\pi-p\pi$  bonding decreases going from  $BF_3$  to  $BBr_3$  and thus Lewis acidic nature increases in the order :



(c) **Al and Ga are trivalent in their compounds but in case of Tl, monovalent compounds are the most stable. Why ?**

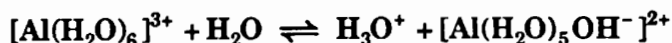
- It is due to 'inert pair' effect due to which stability of +3 state decreases and that of +1 state increases while going down the group (in this case group 13).



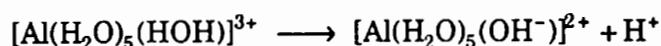
(d)  **$BF_3$  reacts with  $F^-$  to give  $BF_4^-$ , but  $AlF_3$  reacts with  $F^-$  to give  $AlF_6^{3-}$ .**

- Boron has only  $2s$  and  $2p$  valence orbitals and can form maximum of four bonds. Aluminium has available  $3d$ -orbitals and can use octahedral  $sp^3d^2$ -hybrid orbitals to bond to six  $F^-$  ions.

(e) **Aqueous solutions of aluminium salts are acidic**

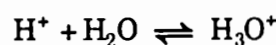


- Due to attractive power of the small, highly charged  $Al^{3+}$  ion for electron, an O—H bond in a ligand  $H_2O$  molecule breaks thus releasing a proton to an  $H_2O$  molecule outside the coordination sphere. Thus,  $H_2O$  ligand is converted to  $OH^-$ , and the complex ion to  $[Al(H_2O)_5OH]^{2+}$

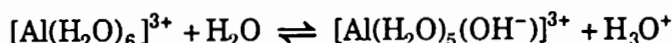


One of  $H_2O$  ligands releases  $H^+$

(which goes to  $H_2O$  solvent) and  $OH^-$   
(which remains as ligand in complex)



Thus, net reaction is



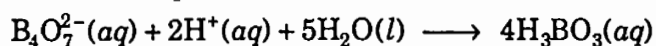
Thus aqueous  $Al^{3+}$  salts are acidic.

# Master Exercises

## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

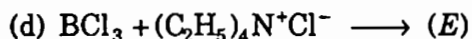
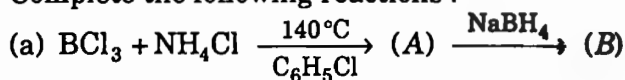
1. Rewrite the equation :



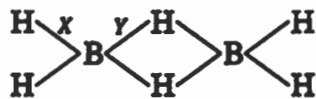
showing the reaction as one that involves the  $\text{B}_4\text{O}_5(\text{OH})_2^{2-}$  ion instead of  $\text{B}_4\text{O}_7^{2-}$ . Does it matter very much which equation is used?

2. Aqueous solution of borax containing one mole of it reacts with two moles of acid. Explain.
3. Borax is also used as a buffer. Explain.
4.  $\text{H}_3\text{BO}_3$  can't be titrated satisfactorily with  $\text{NaOH}$ , why?
5. (a) The formula of boric acid does not represent its structure. What is its formula?  
(b) The formula could be written in a different way. What is it?  
(c) How might you classify 'boric acid' if this formula were used?

6. Complete the following reactions :



7. What are bond order of B—H bonds (X) and (Y) in diborane?



8. Boron-nitride is also called 'inorganic graphite' and borazine is also called inorganic benzene'. Why?
9.  $\text{Al}(\text{OH})_3$  finds uses in 'fire extinguisher' and in 'dyeing'. Explain.

10. Hot  $\text{Al}_2\text{O}_3$  will catalyse the decomposition of ethanol. A colourless gas is given off, which decolorises  $\text{Br}_2$  water. What are the products of the reaction?

11.  $\text{AlCl}_3$  can be converted into  $\text{AlCl}$ . What are the necessary conditions?

12. (A)  $\xrightarrow[\text{aq BaCl}_2]{\text{NaOH, } \Delta}$  gas (B) giving white fumes with  $\text{HCl}$  alongwith white ppt (D) which dissolves in excess of  $\text{NaOH}$  to give (E)  
white ppt (C)

0.453g of (A) gave 0.466g of (C).  $\text{H}_2\text{O}$  content in (A) is 47.68%.

Identify (A), (B), (C), (D) and (E), and explain reactions.

13. Which type of cations are capable of replacing aluminium in alums? Give examples.

### Analytical Questions

1. Explain :

- (i)  $\text{BCl}_3$  exists as a monomer whereas  $\text{AlCl}_3$  is a dimer.  
(ii)  $\text{Al}$  forms  $[\text{AlF}_6]^{3-}$  but  $[\text{BF}_6]^{3-}$  is not formed.  
(iii) Boric acid is a weak acid but it can be titrated as a strong acid in presence of ethylene glycol.

2. Some baking powders contain the solids  $\text{NaHCO}_3$  and  $\text{NaAl}(\text{SO}_4)_2$ . When water is added to this mixture of compounds,  $\text{CO}_2(\text{g})$  and  $\text{Al}(\text{OH})_3(\text{s})$  are two of the products. Write the chemical equations to represent this change.

3. In the purification of bauxite ore as a preliminary step in the production of aluminium,  $[\text{Al}(\text{OH})_4]^- (\text{aq})$  can be converted to  $\text{Al}(\text{OH})_3(\text{s})$  by passing  $\text{CO}_2(\text{g})$  through it. Write an equation for the same. Can  $\text{HCl}$  be used instead of  $\text{CO}_2$ ?

4. Which of the following compounds are molecular, and which have an extended three-dimensional structure?

- (a)  $B_2H_6$  (b)  $KAlSi_3O_8$   
(c)  $SO_3$  (d)  $GeCl_4$
5. Which oxide in each of the following pairs is more acidic?  
(a)  $Al_2O_3$  or  $P_4O_{10}$  (b)  $B_2O_3$  or  $Ga_2O_3$   
(c)  $SO_2$  or  $SnO_2$
6. Identify the group 13 (IIIA) element that best fits each of the following descriptions:  
(a) has an unusually low melting point,  
(b) is the most electronegative,  
(c) is the extremely toxic,  
(d) forms an acidic oxide,  
(e) is the most abundant element of the group,  
(f) is the most stable in +1 oxidation state,  
(g) is a semiconductor,  
(h) forms a molecular fluoride.

### NCERT Problems

1. Write balanced equations for the reaction of elemental boron with elemental chlorine, oxygen and nitrogen at high temperature.

2. Why are boron halides are diborane referred to as "electron deficient compounds?"
3. Write the structure of diborane and explain the nature of bonding in it.
4. What happens when a borax solution is acidified? Write a balanced equation for the reaction.
5. Describe what happens when boric acid is heated?
6. Describe briefly how elemental boron can be prepared?
7. Describe the shapes of  $BF_3$  and  $BH_4^-$ . What type of hybridisation can we assign to boron in each of these compounds?
8. Why do boron halides form "addition compounds" with amines?
9. By means of a balanced chemical equation show how  $B(OH)_3$  behaves as an acid in water.

## Exercise 2

### (Stage 2 : High Skill Problem Solving)

#### Only One Option Correct

1. Select incorrect statements.  
(a)  $B_2H_6$  has all B—H bond equal  
(b)  $AlH_3$  is colourless solid and is polymeric containing Al—H—Al bridges  
(c)  $LiAlH_4$  is ionic compound  
(d)  $AlX_3$  ( $X = Cl, Br, I$ ) have low melting point, are covalent and have the halogen-bridged dimeric structure
2. Select correct statements.  
(a) Hydrides of B and Si are volatile and catches fire on exposure to air  
(b) Oxides of B and Si ( $B_2O_3$  and  $SiO_2$ ) are acidic in nature  
(c) Borates and silicates have tetrahedral  $BO_4$  and  $SiO_4$  structural units  
(d) All the above are correct statements
3. NaOH can't be stored in  
(a) Al vessel (b) Zn vessel  
(c) Both (a) & (b) (d) None of these
4. The dipole moments of the given molecules are such that  
(a)  $BF_3 > NF_3 > NH_3$  (b)  $NF_3 > BF_3 > NH_3$   
(c)  $NH_3 > NF_3 > BF_3$  (d)  $NH_3 > BF_3 > NF_3$

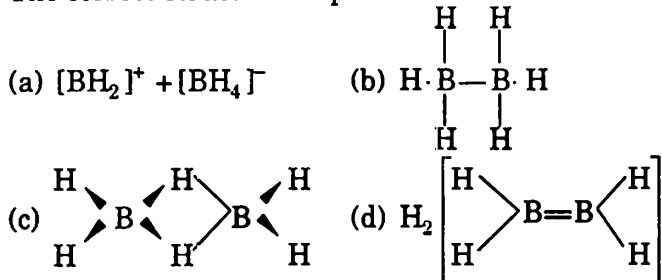
5. Consider the following boron halides

1.  $BF_3$  2.  $BCl_3$   
3.  $BBr_3$  4.  $BI_3$

The Lewis acid characters of these halides are such that

- (a)  $1 < 2 < 3 < 4$  (b)  $1 < 3 < 2 < 4$   
(c)  $4 < 3 < 2 < 1$  (d)  $4 < 2 < 3 < 1$

6. The correct structural representation of diborane is



7. Consider the following statements for diborane

1. Boron is approximately  $sp^3$  hybridized.  
2. B—H—B angle is  $180^\circ$   
3. There are two terminal B—H bonds for each boron atom.  
4. There are only 12 bonding electrons available.
- Of these statements:  
(a) 1,2 and 4 are correct (b) 1,2 and 3 are correct  
(c) 2,3 and 4 are correct (d) 1,3 and 4 are correct

8. Molecule(s) possessing three-centre-two electron bonds and three-centre-four electron bonds would include  
 (a)  $B_2H_6$  and  $SiF_4$  (b)  $XeF_6$  and  $BF_6$   
 (c)  $B_2H_6$  and  $XeF_6$  (d)  $B_2H_6$  alone
9. Which of the following has the regular tetrahedral structure?  
 (a)  $BF_4^-$  (b)  $SF_4$   
 (c)  $XeF_4$  (d)  $[Ni(CN)_4]^{2-}$
10.  $H_3BO_3$  and  $HBO_2$  do not differ in  
 (a) oxidation number (b) basicity  
 (c) melting point (d) structure
11. Light-emitting diodes (LED), laser-diodes and memory chips of computers are made of  
 (a) gallium (b) aluminium  
 (c) arsenic (d) gallium-arsenide
12. Indium is used  
 (a) to dope crystals to make *p-n-p* transistors  
 (b) in thermistors  
 (c) in low melting point solder  
 (d) all the above are correct
13. When boron is fused with  $NaOH$ , products formed are  
 (a)  $Na_2B_4O_7$  and  $H_2$  (b)  $NaBO_2$  and  $H_2$   
 (c)  $Na_3BO_3$  and  $H_2$  (d)  $B_2O_3$  and  $H_2$
14. Thermite welding uses  $Al$  because of  
 (a) its low melting point  
 (b) its lightness  
 (c) its greater affinity for oxygen  
 (d) all the properties given above
15. Consider following reactions  
 I :  $ZnO + C \longrightarrow Zn + CO$   
 II :  $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$   
 III :  $Al_2O_3 + 2Cr \longrightarrow Cr_2O_3 + 2Al$   
 In this, possible reactions are  
 (a) I, III (b) II, III  
 (c) I, II (d) I, II, III
16. Diborane is a Lewis acid forming addition compound  $B_2H_6 \cdot 2NH_3$  with  $NH_3$ , a Lewis base. This  
 (a) is ionic and exists as  $[BH_2(NH_3)_2]^+$  and  $[BH_4]^-$  ions  
 (b) on heating, is converted into borazine,  $B_3N_3H_6$  (called inorganic benzene)  
 (c) both (a) and (b) are correct  
 (d) none of the above is correct
17.  $Al_2(SO_4)_3$  is used in the following but not  
 (a) as a coagulant and precipitant in treating drinking water and sewage  
 (b) in paper industry  
 (c) as a mordant in dyeing  
 (d) in plastic industry
18. General formula of aluminium alums is  
 ( $M^I$  is monovalent cation)  
 (a)  $[M^I(H_2O)_6][Al(H_2O)_6](SO_4)_2$   
 (b)  $[M^I(H_2O)_4][Al(H_2O)_6](SO_4)_2$   
 (c)  $[M^I(H_2O)_4][Al(H_2O)_4](SO_4)_4$   
 (d)  $[M^I(H_2O)_6][Al(H_2O)_6](SO_4)_4$
19. Aqueous solution of borax reacts with 2 moles of acids. This is because of  
 (a) formation of 2 moles of  $B(OH)_3$  only  
 (b) formation of 2 moles of  $[B(OH)_4]^-$  only  
 (c) formation of 1 mole each of  $B(OH)_3$  and  $[B(OH)_4]^-$   
 (d) formation of 2 moles each of  $[B(OH)_4]^-$  and  $B(OH)_3$ , of which only  $[B(OH)_4]^-$  reacts with acid
20. Borax is used as a buffer since  
 (a) its aqueous solution contains equal amount of weak acid and its salt  
 (b) it is easily available  
 (c) its aqueous solution contains equal amount of strong acid and its salt  
 (d) statement that borax is a buffer, is wrong
21. While testing  $BO_3^{3-}$ , there is green-edged flame on heating the salt with conc.  $H_2SO_4$  and  $CH_3OH$ . Green colour is of  
 (a)  $(CH_3)_3B$  (b)  $(CH_3O)_3B$   
 (c)  $B_2O_3$  (d)  $H_3BO_3$
22. Which is insoluble in excess of  $NH_4OH$ ?  
 (a)  $Al(OH)_3$  (b)  $Cu(OH)_2$   
 (c)  $Zn(OH)_2$  (d)  $Cd(OH)_2$
23. Borax is converted into  $B$  by steps  

$$\text{Borax} \xrightarrow{I} H_3BO_3 \xrightarrow{\Delta} B_2O_3 \xrightarrow{II} B$$
  
 I and II reagents are  
 (a) acid,  $Al$  (b) acid,  $C$   
 (c) acid,  $Fe$  (d) acid,  $Mg$
24. Boron carbide is used  
 (a) in nuclear reactor to absorb neutrons  
 (b) as an abrasive  
 (c) as both (a) & (b)  
 (d) as none of the above
25. Borax is used  
 (a) as a flux in brazing and in silver soldering  
 (b) in making enamel  
 (c) in leather tanning  
 (d) in all given above
26. Soda free glass fibre are made of  
 (a)  $H_3BO_3, B_2O_3$  and  $Ca_3(BO_3)_2$   
 (b)  $H_3BO_3, B_2O_3$   
 (c)  $H_3BO_3$   
 (d)  $B_2O_3$
27.  $Na_3AlF_6$  is added to  $Al_2O_3$  to  
 (a) improve the electrical conductivity of the cell

- (b) increases rate of production  
(c) increase the melting point  
(d) decrease the electrical conductivity
28.  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \xrightarrow{\Delta} \text{NaBO}_2 + (\text{A}) + \text{H}_2\text{O}$   
 $(\text{A}) + \text{MnO} \xrightarrow{\Delta} (\text{B})$   
 (A) and (B) are  
 (a)  $\text{Na}_3\text{BO}_3$ ,  $\text{Mn}_3(\text{BO}_3)_2$   
 (b)  $\text{Na}_2(\text{BO}_2)_2$ ,  $\text{Mn}(\text{BO}_2)_2$   
 (c)  $\text{B}_2\text{O}_3$ ,  $\text{Mn}(\text{BO}_2)_2$   
 (d) none of the above is correct
29. Mixture of  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  can be separated by  
 (a)  $\text{HCl}$  (b)  $\text{NH}_4\text{OH}$   
 (c)  $\text{NaOH}$  (d)  $\text{HNO}_3$
30. Boric acid is the trivial name for  
 (a) orthoboric acid (b) metaboric acid  
 (c) pyroboric acid (d) none of these
31. In  $\text{H}_2\text{O}$ ,  $\text{Ga}^+$  changes to  
 (a)  $\text{Ga}^{3+}$  (b)  $\text{Ga}$   
 (c)  $\text{Ga}$  and  $\text{Ga}^{3+}$  (d)  $\text{Ga}^{2+}$  and  $\text{Ga}^{3+}$
32.  $\text{Al}^{3+}$  of  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (alum) can be replaced by  
 (a)  $\text{Cr}^{3+}$  (b)  $\text{Co}^{3+}$   
 (c)  $\text{Fe}^{3+}$  (d) all of these
33. Borax  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  is actually  
 (a)  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$   
 (b)  $\text{Na}_2[\text{B}_4\text{O}_4(\text{OH})_6] \cdot 7\text{H}_2\text{O}$   
 (c)  $\text{Na}_2[\text{B}_4\text{O}_3(\text{OH})_8] \cdot 6\text{H}_2\text{O}$   
 (d)  $\text{Na}_2[\text{B}_4\text{O}_2(\text{OH})_{10}] \cdot 5\text{H}_2\text{O}$
34. Which reactions can be used to prepare diborane  
 I.  $\text{NaBH}_4 + \text{BF}_3$  (in ether)  $\longrightarrow$   
 II.  $\text{NaBH}_4 + \text{I}_2 \longrightarrow$   
 III.  $\text{BF}_3 + \text{NaH} \longrightarrow$   
 (a) I, III (b) I, II  
 (c) II, III (d) I, II and III
35. Which of the following statements about  $\text{H}_3\text{BO}_3$  is not correct?  
 (a) It is strong tribasic acid  
 (b) It is prepared by acidifying an aqueous solution of borax  
 (c) It has a layer structure in which planar  $\text{BO}_3$  units are joined by hydrogen bonds  
 (d) It does not act as a Lewis acid by accepting hydroxyl ion
36. The type of hybridisation of boron in diborane is  
 (a)  $sp$  (b)  $sp^2$   
 (c)  $sp^3$  (d)  $sp^3d^2$
37. Reactivity of borazole is greater than that of benzene because  
 (a) borazole is polar compound  
 (b) borazole is non-polar compound  
 (c) borazole is electron deficient compound  
 (d) of localised electrons in it
38. Arsenic drugs are mainly used for the treatment of  
 (a) cholera (b) typhoid  
 (c) jaundice (d) syphilis
39.  $\text{B}(\text{OH})_3 + \text{NaOH} \rightleftharpoons \text{NaBO}_2 + \text{Na}[\text{B}(\text{OH})_4] + \text{H}_2\text{O}$   
 How can this reaction be made to proceed in forward direction?  
 (a) Addition of *cis*-1,2-diol  
 (b) Addition of borax  
 (c) Addition of *trans*-1,2-diol  
 (d) Addition of  $\text{Na}_2\text{HPO}_4$
40.  $\text{H}_3\text{BO}_3$  is  
 (a) monobasic acid and weak Lewis acid  
 (b) monobasic and weak Bronsted acid  
 (c) monobasic and strong Lewis acid  
 (d) tribasic and weak Bronsted acid
41.  $\text{AlCl}_3$  fumes in moist air because it  
 (a) is covalent (b) is volatile  
 (c) is hygroscopic (d) forms  $\text{HCl}$  in moist air
42. The solution of sodium meta aluminate on boiling with ammonium chloride gives a white precipitate of  
 (a)  $\text{Al}_2\text{O}_3$  (b)  $\text{AlCl}_3$   
 (c)  $\text{Al}(\text{OH})_3$  (d)  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3$
43. The incorrect statement is  
 (a) Anhydrous  $\text{AlCl}_3$  is a covalent substance  
 (b) Ionic compounds generally have low melting point and boiling point.  
 (c) A molecule shows a more stable form as compared to individual atom  
 (d)  $\text{CCl}_4$  is a non-polar solvent
44. Which of the following has the highest first ionisation energy?  
 (a) Lithium (b) Beryllium  
 (c) Boron (d) Carbon
45. Fusion of borane with  $\text{NaOH}$  produces  
 (a)  $\text{B}_2\text{O}_3 + \text{H}_2\text{O}$  (b)  $\text{NaBO}_2 + \text{H}_2\text{O}$   
 (c)  $\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_2\text{O}$  (d)  $\text{Na}_3\text{BO}_3 + \text{H}_2\text{O}$
46. Radius of Ga is less than Al because of  
 (a) lanthanoid contraction  
 (b) greater screening effect  
 (c) inert pair effect  
 (d) None of the above
47. In the reaction  $\text{B}_2\text{O}_3 + \text{C} + \text{Cl}_2 \longrightarrow \text{A} + \text{CO}$   
 A is  
 (a)  $\text{BCl}_2$  (b)  $\text{B}_2\text{Cl}_2$   
 (c)  $\text{CCl}_2$  (d)  $\text{BCl}_3$
48. Which of the following compounds is/are possible?  
 (a)  $\text{B}_2\text{Cl}_4$ ,  $\text{BCl}_2$ ,  $\text{Cl}_2\text{B}$  (b)  $\text{GaCl}_2$ ,  $\text{GaS}$   
 (c)  $\text{Ga}[\text{GaCl}_4] \cdot \text{Ga}_2\text{S}_2$  (d) All of these

49. Diamagnetic species can be  
 (a)  $B_2Cl_4$  (b)  $GaCl_2$   
 (c)  $GaS$  (d) all of these
50. Which of the following are used as transition materials and light-emitting devices (LED)?  
 I : Gallium-phosphides  
 II : Indium-phosphides  
 III : Gallium-arsenides  
 IV : Indium-arsenides  
 (a) All (b) Except I all  
 (c) Except I, II all (d) Only IV
51. Select correct statement(s).  
 (a) Aluminium dissolves in dilute mineral acids but is made passive by concentrated nitric acid  
 (b) Aluminium vessel can be used as storage of NaOH  
 (c) Both of the above  
 (d) None of the above
52. Thallium and lead are classified as chemically soft because  
 (a) they have higher affinities for soft anions as  $I^-$  and  $S^{2-}$  ions  
 (b) they are soft in reactivity  
 (c) they are stable in lower oxidation state ( $Tl^+$ ,  $Pb^{2+}$ )  
 (d) they are stable in higher oxidation state ( $Tl^{3+}$ ,  $Pb^{4+}$ )
53. The relative stability of the different oxidation state  
 $Tl^+ > Tl^{3+}$ ,  $Ga^{3+} > Ga^+$   
 $Tl^+ > In^+ > Ga^+$   
 is an example of  
 (a) redox potential (b) disproportionation  
 (c) inert pair effect (d) electron-affinity
54. Thermal stability of boron compounds is in order  
 (a)  $B_2F_4 < B_2Cl_4 < B_2(OR)_4 < B_2(NR_2)_4$   
 (b)  $B_2Cl_4 < B_2F_4 < Br(OR)_4 < B_2(NR_2)_4$   
 (c)  $B_2(NR_2)_4 < B_2(OR)_4 < B_2Cl_4 < B_2F_4$   
 (d)  $B_2(NR_2)_4 < B_2(OR)_4 < B_2F_4 < B_2Cl_4$
55. Anion containing both three- and four-coordinated boron is  
 (a)  $[B(OH)_4]^-$  (b)  $B_3O_6^{3-}$   
 (c)  $[B_4O_5(OH)_4]^{2-}$  (d)  $BO_3BO_4^{4-}$
56. Which is spontaneous in forward side?  
 (a)  $Al^{3+} + 2e^- \longrightarrow Al^+$  (b)  $Ga^{3+} + 2e^- \longrightarrow Ga^+$   
 (c)  $In^{3+} + 2e^- \longrightarrow In^+$  (d)  $Tl^{3+} + 2e^- \longrightarrow Tl^+$
57. Light elements B, Al, C and Si are  
 (a) oxophiles (high affinity for oxygen)  
 (b) fluorophiles (high affinity for fluorine)  
 (c) both type  
 (d) none of the types given
58. Stabilities of adducts formed with boron-halides is in order  
 (a)  $BF_3 < BCl_3 < BBr_3$  (b)  $BBr_3 < BCl_3 < BF_3$   
 (c)  $BCl_3 < BBr_3 < BF_3$  (d)  $BF_3 < BBr_3 < BCl_3$
59. The thermal disproportionation of  $B_2Cl_4$  gives  
 (a)  $BCl_3$  (b)  $B_4Cl_4$   
 (c)  $B_8Cl_8$  (d) all of these
60. Boric acid is a weak acid. Thus, it behaves as  
 (a) proton donor as in  

$$H_3BO_3 + H_2O \rightleftharpoons H_3O^+ + H_2BO_3^-$$
  
 (b) an electron acceptor as in  

$$B(OH)_3 + H_2O \rightleftharpoons [B(OH)_4]^- + H^+$$
  
 (c) proton acceptor as in  

$$H_3BO_3 + H_2O \rightleftharpoons H_4BO_3^+ + OH^-$$
  
 (d) an electron donor as in  

$$H_3BO_3 \rightleftharpoons H_3BO_3^+ + e^-$$
61. The decrease stability of higher oxidation state in  $p$ -block with increasing atomic number is due to  
 (a) decrease in bond energy as going down the group  
 (b) energy required to unpair  $ns^2$  electrons is not compensated by the energy released in forming the two additional bonds  
 (c) both (a) and (b) are correct  
 (d) none of the above is correct
62. Select correct statement(s) about group 13 (IIIA) elements.  
 (a) Stability of hydrides ( $MH_3$ ) decreases as we move down the group  
 (b)  $MX_3$  is a strong Lewis acid  
 (c)  $[Al(H_2O)_6]^{3+}$  exists in aqueous solution  
 (d) All the above are correct statements
63.  $AlO_2^-$  is known as  
 (a) aluminium dioxo ion (b) meta aluminate ion  
 (c) dioxo aluminium ion (d) aluminium oxide ion
64. In aqueous solution  $GaCl$  disproportionates to  
 (a)  $GaCl_2$  and  $GaCl_3$  (b)  $Ga$  and  $GaCl_3$   
 (c)  $GaCl_2$  and  $Ga$  (d)  $GaCl_3$  and  $GaCl_5$
65. Boron does not form  $B^{3+}$  cation easily. It is due to  
 (a) energy required to form  $B^{3+}$  ion is for more than that which would be compensated by lattice energies or hydration energies of such ion  
 (b) boron is non-metal  
 (c) boron is semiconductor  
 (d) none of the above
66. An alloy of boron and aluminium is allowed to react with  $NH_3$ . Products formed are  
 (a)  $BN$ ,  $AlN$  and  $H_2$   
 (b)  $B(NH_2)_3$ ,  $Al(NH_2)_3$  and  $H_2$   
 (c)  $BN$ ,  $Al(NH_2)_3$  and  $H_2$   
 (d)  $B(NH_2)_3$ ,  $AlN$  and  $H_2$
67. Element  $M + N_2 \xrightarrow{\Delta} \xrightarrow{H_2O} NH_3$   
 Element  $M$  belonging to group 13 can be  
 (a) B or Al (b) Ga or Al  
 (c) Mg or Al or B (d) Mg or B

58.  $N_2$  gas is passed or heated Mg and B. Products formed are  
 (a)  $Mg_3N_2$ , BN (b)  $Mg_3N_2$ , BN and  $Mg_3B_2$   
 (c)  $MgN$ , BN (d) no reaction
69. Anodising can be done by electrolysis of dilute  $H_2SO_4$  with Al as anode. This results in  
 (a) the formation of protective oxide layer ( $Al_2O_3$ )  
 (b) the formation of  $Al_2(SO_4)_3$  and  $SO_2$  gas  
 (c) the formation of  $AlH_3$  and  $SO_2$  gas  
 (d) the formation of  $Al(HSO_3)_3$  and  $H_2$  gas
70. Alzheimer's disease is caused due to Al interaction with internal organs of the body if food is contaminated with Al. This disease  
 (a) induces senility in young persons  
 (b) causes memory loss  
 (c) both (a) and (b) are correct  
 (d) none of the above is correct
71. Pure boron is best prepared by  
 (a) heating  $B_2O_3$  with  $H_2$   
 (b) heating  $B_2O_3$  with Na or K  
 (c) heating  $KBF_4$  with Na or K  
 (d) heating  $BBr_3$  with  $H_2$  in presence of a catalyst
72. The borax bead test can be used to detect the presence of  
 (a)  $Al^{3+}$  (b)  $Mg^{2+}$   
 (c)  $Fe^{3+}$  (d)  $Na^+$
73. Water softener is  
 (a) borax (b) zeolite  
 (c) both (a) and (b) (d) none of these
74.  $Na_2B_4O_7 \cdot 10H_2O$  is correctly represented as  
 (a)  $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$   
 (b)  $2NaBO_2 \cdot Na_2B_2O_3 \cdot 10H_2O$   
 (c)  $Na_2[B_4(H_2O)_4O_7] \cdot 6H_2O$   
 (d) all of the above
75. B can be obtained from halide by van Arkel method. This involves reaction  
 (a)  $2BCl_3 + 3H_2 \xrightarrow[\text{filament}]{\text{red hot W or Ta}} 2B + 6HCl$   
 (b)  $2BI_3 \xrightarrow{\text{red hot W or Ta}} 2B + 3I_2$   
 (c) both (a) and (b)  
 (d) none of the above
76. Which of the following statements regarding orthoboric acid ( $H_3BO_3$ ) is false?  
 (a) It acts as a monobasic acid  
 (b) It is soluble in hot water  
 (c) It has a planar structure  
 (d) It acts as a tribasic acid
77. When orthoboric acid is heated to red heat the residue is  
 (a) boron (b) boric oxide  
 (c) metaboric acid (d) pyroboric acid
78. Orthoboric acid  $H_3BO_3$  behaves as weak monobasic acid giving  $H_3O^+$  and  
 (a)  $H_2BO_2^+$  (b)  $H_2BO_2^-$   
 (c)  $[B(OH)_4]^-$  (d)  $[B(OH)_4]^+$
79. Boron sesquioxide is  
 (a)  $B_2O_3$  (b)  $BO_3$   
 (c)  $BO_3^{3-}$  (d)  $BO_2^-$
80. Select correct statement(s) about  $H_3BO_3$   
 (a) It has triangular  $BO_3^{3-}$  units  
 (b) In solid states, molecules are hydrogen bonded  
 (c) Both (a) & (b) are correct  
 (d) None of the statements is correct
81. The structure of  $BF_3$  is  
 (a) tetrahedral (b) pyramidal  
 (c) planar triangular (d) T-shaped
82. In  $BF_3$   
 (a) all the B—F bond are single covalents in nature  
 (b) boron-fluorine bond has some double bond character and this bond is delocalised  
 (c) bond energy and bond length of B—F bond indicate its single bond character  
 (d) all the bonds are ionic
83.  $BF_3$  behaves as a  
 (a) Lewis acid and lone pair from the Lewis base is filled into empty  $2p_z$  orbital  
 (b) Lewis base and lone pair on B is donated to empty orbital of the Lewis acid  
 (c) amphoteric species due to interaction with acid and base both  
 (d) polymer substance
84.  $B_2Cl_4$   
 (a) can be formed by passing  $BCl_3$  over Hg at low pressure in an electric discharge  
 (b) can exist on non-eclipsed and planar structure  
 (c) decomposes at low temperature  
 (d) can show all the facts given above
85.  $BF_3$  on hydrolysis forms  
 (a)  $H_3BO_3$  (b)  $HBFO_4$   
 (c) both (a) and (b) (d) None of these
86. Which of the following is false statement?  
 (a)  $BH_3$  is a Lewis acid  
 (b) All the B—H distance in diborane ( $B_2H_6$ ) are equal  
 (c) Boranes are easily hydrolysed  
 (d)  $LiAlH_4$  reduces  $BCl_3$  to borane
87. In  $B_2H_6$   
 (a) there is direct boron-boron bond  
 (b) the B—H bonds are ionic  
 (c) it is isostructural to  $C_2H_6$   
 (d) boron atoms are linked through hydrogen bridges



88. From  $B_2H_6$  all the following can be prepared except  
 (a)  $H_3BO_3$  (b)  $NaBH_4$   
 (c)  $B_2(CH_3)_6$  (d)  $B_2O_3$
89. Boron nitride has the structure of the type  
 (a) both diamond and graphite  
 (b) graphite  
 (c) diamond  
 (d) NaCl
90. Which of the following is the false statement?  
 (a) Reducing action of  $NaBH_4$  and  $LiAlH_4$  are specific  
 (b)  $B_2H_6$  reduces alkene to primary alcohol  
 (c) Both (a) and (b) are the false statements  
 (d) None of the above is false statement.
91. Beryllium and aluminium have similar properties because  
 (a) they belong to same group  
 (b) they have different electronegativity  
 (c) they have same electronegativity  
 (d) they have same ionisation energy
92. The solubility of  $Al(OH)_3$  in strong NaOH solution is best explained by the formation of  
 (a)  $AlO_2^-$  ion  
 (b) double salt  
 (c) a peptised colloidal sol  
 (d) a complex hydroxyl aluminate ion
93. On passing  $CO_2$  into aqueous solution containing  $Al^{3+}$   
 (a)  $Al_2(CO_3)_3$  is formed  
 (b)  $Al(OH)_3$  is precipitated  
 (c)  $[Al(OH)_4]^-$  is formed  
 (d) colloidal  $Al(OH)_3$  is formed
94. Addition of sodium carbonate to a solution of an oxide in water produces  $CO_2$ . This experiment indicates that  
 (a) the oxide is that of a non-metal  
 (b) the oxide is basic  
 (c) the oxide is amphoteric  
 (d) the oxide is neutral
95. Dimer formation can take place with  
 (a)  $BH_3$  (b)  $AlCl_3$   
 (c)  $NO_2$  (d) all of these
96. The major constituent in cement is  
 (a) silica (b) magnesium oxide  
 (c) calcium carbonate (d) iron oxide
97. Hardening of cement is due to  
 (a) dehydration  
 (b) hydrolysis  
 (c) hydration and hydrolysis  
 (d) polymerisation
98. Alums are used as mordant in dyeing because  
 (a) dye is adsorbed on  $Al(OH)_3$  which is deposited on fibre in the hydrolysis process  
 (b) dye is adsorbed on KOH formed due to hydrolysis  
 (c) of both (a) and (b)  
 (d) of none of the above
99. Alum is found to contain hydrated monovalent cation  $[M(H_2O)_6]^+$ , trivalent cation  $[M'(H_2O)_6]^{3+}$  and  $SO_4^{2-}$  in the ratio of  
 (a) 1:1:1 (b) 1:2:3  
 (c) 1:3:2 (d) 1:1:2
100. About 2 to 5% of gypsum ( $CaSO_4 \cdot 2H_2O$ ) is added to Portland cement. It is just to  
 (a) increase the setting rate of the cement during hydration  
 (b) slow down the setting rate to increase strength during hydration  
 (c) both (a) and (b) are correct  
 (d) none of the above is correct

### One or More Than One Options Correct

1. Which fumes in moist air?  
 (a)  $AlCl_3$  (b)  $BF_3$   
 (c)  $CuSO_4$  (d)  $NH_3$
2. Select correct statement(s).  
 (a)  $BF_3$  fumes strongly in moist air and is partially hydrolysed by excess of water  
 (b)  $BF_3$  is converted into the adducts  $BF_3 \cdot H_2O$  and  $BF_3 \cdot 2H_2O$  with small amounts of water at low temperature  
 (c)  $H_3BO_3$  is a weak acid but  $HBF_4$  is a very strong acid  
 (d)  $KBF_4$  is sparingly soluble in water
3. Select correct statement(s).  
 (a)  $BF_3$  forms adducts with  $NH_3$ ,  $ROH$  and  $RNH_2$   
 (b)  $BCl_3$  form adducts with  $NH_3$ ,  $H_2O$  and  $RNH_2$   
 (c)  $BCl_3$  reacts with liquid  $NH_3$  and ethanol forming  $B(NH_2)_3$  and  $B(OEt)_3$   
 (d)  $[BCl_4]^-$ ,  $[BBr_4]^-$  and  $[BI_4]^-$  ions can be made only in non-aqueous media
4. Select correct statement(s).  
 (a) Boron trimethyl is a weaker Lewis acid than the boron trihalides or monoborane  
 (b) Lewis acid property when  $Me_3N$  is a donor is in order :  

$$BBr_3 > BCl_3 > BF_3 \sim BH_3 > BMe_3$$
  
 (c) Lewis acid property when  $Me_3P$  is a donor is in order :  

$$BBr_3 > BCl_3 \sim BH_3 > BF_3 \sim BMe_3$$
  
 (d) Lewis acid property when CO is a donor : no adduct is formed with halides and Lewis acid property of  

$$BH_3 \gg BF_3 \cdot BMe_3$$

5. Select correct statement(s).

- (a) A saturated solution of boric acid in water is neutral to the indicator bromocresol green
- (b)  $\text{AlF}_3$  is insoluble in anhydrous  $\text{HF}$
- (c) Aqueous solution of  $\text{KHF}_2$  is basic to the indicator bromocresol green
- (d) Aqueous solution of boric acid and potassium hydrogen difluoride is alkaline to bromocresol indicator

6. Select correct statement(s).

- (a) Diborane is an electron-deficient compound
- (b) Diborane is stoichiometrically analogous to ethane ( $\text{C}_2\text{H}_6$ )
- (c) Total electrons involved in bonding are 12 in diborane and ethane
- (d) Total electrons involved in bonding are 12 in diborane and 14 in ethane

7. Boric acid is a weak Lewis acid proton comes from

- (a) by its ionisation
- (b) when it forms complex with  $\text{H}_2\text{O}$
- (c) when it forms borate esters with alcohol
- (d) all of the above

8. Select correct statement(s).

- (a) On the basis of Lewis acidity, an oxygen atom is more effective than a fluorine atom as a  $\pi$ -donor towards boron
- (b) 1,2-diols have a strong tendency to form borate esters on account of chelate effect
- (c) Borate esters are stable due to chelate effect
- (d) None of the above is correct statement

9. Actual source of protons in boric acid is based on the following

- (a)  $\text{B}(\text{OH})_3(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + [\text{B}(\text{OH})_4]^- (\text{aq})$
- (b)  $3\text{B}(\text{OH})_3(\text{aq}) \rightleftharpoons [\text{B}_3\text{O}_3(\text{OH})_4]^- (\text{aq}) + \text{H}^+(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$   
in neutral or basic solution
- (c)  $\text{B}(\text{OH})_3 \rightleftharpoons \text{H}_2\text{BO}_2^- + \text{H}^+$
- (d) all of the above

10. Select correct statement(s).

- (a) Aluminium monohalides are formed by the reactions of the trihalides with aluminium at 1300K followed by rapid cooling
- (b) Aluminium monochloride (red) is formed when aluminium reacts with  $\text{HCl}$  at 1200 K
- (c) Aluminium monohalides disproportionate at room temperature
- (d)  $\text{Ga}_2\text{Cl}_4$  exists as  $\text{Ga}^+[\text{GaCl}_4]^-$  and is diamagnetic and has crystalline structure.

11. Consider following statements

- I: Boric acid is a mild antiseptic and is used as a food preservative.
- II: Borax and other borates are used in water-treatment, timber preservation, glass manufacture.

III: Sodium peroxoborate is an important constituent of washing powder.

Select correct statement.

- (a) I, II
- (b) II, III
- (c) I, III
- (d) I, II, III

12. Select correct alternate(s).

- (a) The group BN is isoelectronic with  $\text{C}_2$
- (b) No species with  $\text{B}\equiv\text{N}$  group is formed
- (c) Common form of boron nitride has an ordered layer structure closely resembling that of graphite
- (d)  $\text{AlN}$  has the wurtzite structure

## Passage Comprehension Questions

### Passage 1

The tetrafluoroborate anion  $\text{BF}_4^-$ , is a Lewis base. The other tetrahaloborate anions,  $\text{BCl}_4^-$  and  $\text{BBr}_4^-$ , can be prepared in non-aqueous solvents.

Based on the above short write-up, answer the following questions :

1.  $\text{BF}_4^-$  is

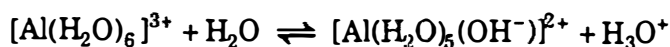
- (a)  $\text{F}^-$  donor
- (b) a lone-pair acceptor
- (c) a lone-pair donor
- (d) solvated in aqueous solution

2.  $\text{BCl}_4^-$  and  $\text{BBr}_4^-$  are stable in

- (a)  $\text{H}_2\text{O}$
- (b) alcohol
- (c) both (a) and (b)
- (d) None of these

### Passage 2

Certain aspects of the aqueous chemistry of aluminium compounds derive from the nature of the hydrated aluminium ion  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ .



Read the above write-up and answer the following questions.

1. Above equilibrium indicates that

- (a)  $\text{H}_2\text{O}$  is a Lowry-Bronsted acid
- (b)  $\text{H}_2\text{O}$  is a Lowry-Bronsted base
- (c)  $\text{H}_2\text{O}$  is a Lowry-Bronsted acid as well as a base
- (d)  $\text{H}_2\text{O}$  is neither acid nor base

2. Above equilibrium is repressed in

- (a) strongly acidic solution
- (b) alkaline solution
- (c) aqueous solution
- (d) any of the above

3. Ionisation of the above equilibrium is favoured in

- (a) strongly acidic solution
- (b) alkaline solution

- (c) aqueous solution  
(d) any of the above
4. Aluminate ion can be written as  
(a)  $\text{AlO}_2^-$  (b)  $\text{Al}(\text{OH})_4^-$   
(c)  $[\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4]^-$  (d) all of these

### Passage 3

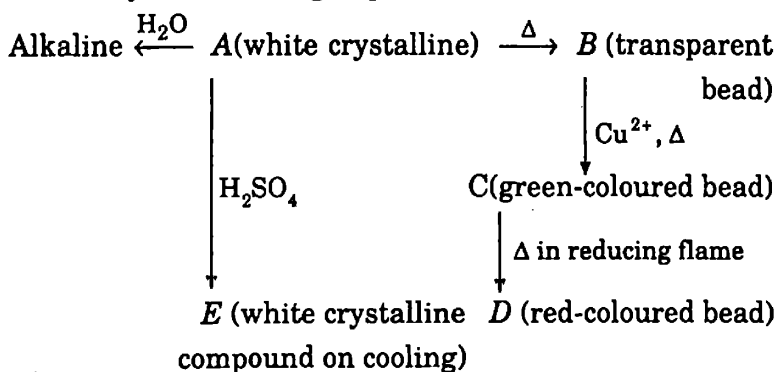
Diborane is an electron deficient compound. Stoichiometrically, it is analogous to ethane,  $\text{C}_2\text{H}_6$ . However, the total number of electrons involved in bonding and less in diborane.

Read the above short note and answer the following questions.

- Bonding electrons involved  
(a) in  $\text{B}_2\text{H}_6$  is 14 and in  $\text{C}_2\text{H}_6$  16  
(b) in  $\text{B}_2\text{H}_6$  is 12 and in  $\text{C}_2\text{H}_6$  14  
(c) in  $\text{B}_2\text{H}_6$  is 10 and in  $\text{C}_2\text{H}_6$  12  
(d) in  $\text{B}_2\text{H}_6$  is 16 and in  $\text{C}_2\text{H}_6$  18
- Octet is complete in  
(a) boron in diborane  
(b) carbon in ethane  
(c) boron in diborane and carbon in ethane  
(d) None of the above
- In diborane there is  
(a) two-electron-three-centre bonds  
(b) three-electron-three-centre bonds  
(c) two-electron-two-centre bonds  
(d) three-electron-two-centre bonds
- Consider the following statements for diborane  
I. Boron is approximately  $sp^3$  hybridised  
II.  $\text{B}-\text{H}-\text{B}$  angle is  $180^\circ$   
III. There are two terminal  $\text{B}-\text{H}$  bonds for each boron atom  
IV. There are only 12 bonding electrons available  
Of these statements  
(a) I, III and IV are correct  
(b) I, II and III are correct  
(c) II, III and IV are correct  
(d) I, II and IV are correct

### Passage 4

Study the following sequence of reactions :



- A is  
(a)  $\text{NaBO}_2$  (b)  $\text{Na}_2\text{B}_4\text{O}_7$   
(c)  $\text{H}_3\text{BO}_3$  (d)  $\text{HBO}_3$
- B is  
(a)  $\text{NaBO}_2$  (b)  $\text{B}_2\text{O}_3$   
(c)  $\text{Na}_3\text{BO}_3$  (d)  $\text{H}_3\text{BO}_3$
- C and D respectively are  
(a)  $\text{Cu}_2\text{BO}_2$ ,  $\text{CuO}$  (b)  $\text{Cu}(\text{BO}_2)_2$ ,  $\text{CuBO}_2$   
(c)  $\text{Cu}_2\text{B}_2\text{O}_4$ ,  $\text{CuO}$  (d)  $\text{Cu}(\text{BO}_2)_2$ ,  $\text{Cu}_2\text{B}_2\text{O}_4$
- Select correct statement(s) about E  
(a) E is a weak acid ( $\text{H}_3\text{BO}_3$ )  
(b) It is not a protonic acid but electron-pair acceptor  
(c) E shows following equilibrium  

$$\text{B}(\text{OH})_3 + \text{H}_2\text{O} \rightleftharpoons [\text{B}(\text{OH})_4]^- + \text{H}_3\text{O}^+$$
  
(d) All the above are correct statements

### Passage 5

The chemical properties of boron, carbon, silicon and germanium are distinctly those of non-metals. The light elements, boron, aluminium, carbon and silicon are strong oxophiles and fluorophiles, in the sense that they have high affinities for oxygen and fluorine, respectively.

Based on the above short write-up, answer the following questions.

- Oxophilic character is observed in  
(a) borates, aluminates, carbonates, silicates  
(b) boranes, alkanes, silanes, alanes  
(c) both of the above  
(d) none of the above
- The similar oxophilicity and fluorophilicity concludes that diagonal relationship is between  
(a) boron and aluminium  
(b) boron and silicon  
(c) boron and carbon  
(d) aluminium and silicon

### Assertion & Reason

Codes :

- (a) Both A and R are true and R is the correct explanation of A.  
(b) Both A and R are true but R is not the correct explanation of A.  
(c) A is true but R is false.  
(d) A is false but R is true.

1. Assertion (A) : Boron forms  $\text{BF}_4^-$ .

Reason (R) :  $\text{BF}_3$  is an electron deficient species.

2. Assertion (A) :  $\text{B}_2\text{Cl}_4$ ,  $\text{GaCl}_2$ ,  $\text{GaS}$  are diamagnetic.

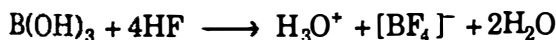
Reason (R) : They show +2 oxidation state.

3. Assertion (A) :  $\text{NaBH}_4$  has NaCl structure.

Reason (R) :  $\text{NaBH}_4$  is an ionic salt.

4. **Assertion (A)** :  $\text{HBF}_4$  is a very strong acid.

**Reason (R)** :  $\text{B(OH)}_3$  behaves as an acid in the following reaction :



5. **Assertion (A)** : Cryolite is added to bauxite in metallurgical extraction of aluminium.

**Reason (R)** : Cryolite,  $\text{Na}_3[\text{AlF}_6]$  contains an octahedrally coordinated aluminium atom.

6. **Assertion (A)** :  $\text{AlCl}_3$  exists as  $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$  in dilute aqueous solution.

**Reason (R)** : When water is dropped to a solid  $\text{AlCl}_3$ , vigorous hydrolysis ensues.

7. **Assertion (A)** :  $\text{B(OH)}_3$  is a good lubricant and slippery.

**Reason (R)** :  $\text{B(OH)}_3$  has a layer structure.

8. **Assertion (A)** : Boric acid does not act as a proton donor but an electron-acceptor.



**Reason (R)** : Boric acid is a very weak acid.

9. **Assertion (A)** : The group BN is isoelectronic with  $\text{C}_2$ .

**Reason (R)** : No species containing a  $\text{B}\equiv\text{N}$  group has yet been discovered.

10. **Assertion (A)** :  $\text{B}_3\text{N}_3\text{H}_{12}$  (similar to cyclohexane) exists as chair conformation.

**Reason (R)** : Borazine ( $\text{B}_3\text{N}_3\text{H}_6$ ) is much more reactive than benzene.

11. **Assertion (A)** : Aluminium trimethyl is a dimer having structure like that of  $\text{AlCl}_3$ .

**Reason (R)** : There is three-centre two-electron bonding in  $\text{Al}-\text{C}-\text{Al}$  bridge.

12. **Assertion (A)** : Borazine is called inorganic benzene.

**Reason (R)** : Borazine undergoes addition and substitution reactions with  $\text{HCl}$  and  $\text{Br}_2$  etc.

13. **Assertion (A)** : The bond lengths in  $\text{BF}_3$  are  $1.30 \text{ \AA}$  and are shorter than the sum of the covalent radii.

**Reason (R)** :  $p\pi-p\pi$  interaction exists and all  $\text{B}-\text{F}$  bonds are equivalent are based on modern explanation, the double bond is delocalised.

14. **Assertion (A)** :  $\text{AlCl}_3$  forms dimer  $\text{Al}_2\text{Cl}_6$  but is dissolves in  $\text{H}_2\text{O}$  forming  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  and  $\text{Cl}^-$  ions.

**Reason (R)** : Aqueous solution of  $\text{AlCl}_3$  is acidic due to hydrolysis.

15. **Assertion (A)** : In aqueous solution  $\text{AlCl}_3$  forms dimer  $\text{Al}_2\text{Cl}_6$ .

**Reason (R)** : The high enthalpy of hydration is sufficient to break the covalent dimer into  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$  and  $\text{Cl}^-$  ions.

16. **Assertion (A)** : In water, orthoboric acid behaves as a weak monobasic acid.

**Reason (R)** : In water orthoboric acid acts as a proton donor.

17. **Assertion (A)** : Boron always forms covalent bond.

**Reason (R)** : The small size of  $\text{B}^{3+}$  favours formation of covalent bond.

## True & False

1. Borosilicate glass has a lower coefficient of thermal expansion.
2.  $\text{H}_3\text{BO}_3$ ,  $\text{B}_2\text{O}_3$  and  $\text{Ca}_3(\text{BO}_3)_2$  are used to make soda-free glass fibre.
3.  $\text{Al}_2\text{O}_3$  is a good conductor.
4. When boron is fused with sodium hydroxide, sodium metaborate ( $\text{NaBO}_2$ ) and hydrogen are formed.
5.  $\text{H}_3\text{PO}_2$  is a weak monobasic acid.
6. Borax is also a good buffer.
7. Metaborate beads of many transition metals have characteristic colours.
8.  $\text{H}_3\text{BO}_3$  is not a Bronsted acid but Lewis acid and accepts  $\text{OH}^-$ .
9.  $\text{NaH}_2\text{PO}_2$  and  $\text{NaHPO}_3$  are acid salts.
10. Borazine  $\text{B}_3\text{N}_3\text{H}_6$  is called inorganic benzene.
11. In diborane all the  $\text{B}-\text{H}$  bonds are equivalent.
12. Structure of aluminate ion changes with both pH and concentration.
13.  $\text{Al(OH)}_3$  is used as mordant in dyeing.
14. In diborane ( $\text{B}_2\text{H}_6$ ) there are  $(2c-2e)$   $(3c-2e)$  type of bonds.
15. Aqueous solution of  $\text{AlCl}_3$  is acidic due to hydrolysis.

## Fill in the Blanks

1. Correct representation of the formula of borax is .....
2. Conversion of  $\text{BI}_3$  into B by pyrolysis is called .....
3. Cryolite ..... the electrical conductivity of  $\text{Al}_2\text{O}_3$  in the extraction of Al.
4. Stability order of  $\text{Ga}^+ < \text{In}^+ < \text{Tl}^+$  is described by .....

5. Concentrated  $\text{HNO}_3$  renders Al passive due to formation of .....
6.  $\text{Al}_2\text{O}_3$  is an ..... oxide.
7.  $\text{H}_3\text{BO}_3$  behaves as .....
8.  $\text{H}_3\text{BO}_3$  does not donate protons but accepts ..... ion.
9. In diborane, boron atom is ..... hybridised.
10.  $\text{S}_2$  is ..... since, it has ..... electrons.
11.  $\text{AlO}$  is formed when aluminium powder is heated in oxygen at  $3260^\circ\text{C}$  and is called .....
12. When ethereal solutions of  $\text{AlCl}_3$  and  $\text{LiAlH}_4$  are mixed, ..... is formed.
13.  $\text{AlCl}_3$  fumes in moisture due to .....
14. When  $\text{AlI}_3$  is heated with  $\text{CCl}_4$ , ..... and ..... are formed.
15. Aluminium chloride forms dimer  $\text{Al}_2\text{Cl}_6$  but in aqueous solution  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  and  $\text{Cl}^-$  ions are formed since, covalent bonds of dimer are broken by .....
16.  $p$ -block elements are characterised by valence shell electronic configuration as .....
17. Boron and aluminium both are amphoteric and form ..... with  $\text{NaOH}$ .
18. Halides of group 13(IIIA) have halogen bridged ..... structures.
19. Reaction of Al with  $\text{O}_2$  is ..... and is called ..... reaction.
20. Use of Al causes disease called .....
21. Borax is used as a ..... standard in titrations against acids.
22.  $\text{B}_2\text{H}_6$  changes  $\text{CH}_3\text{CH}=\text{CH}_2$  with alkaline  $\text{H}_2\text{O}_2$  into .....
23. Diborane ( $\text{B}_2\text{H}_6$ ) has ..... electron bonds.
24.  $\text{Cu}^{2+}$  salts form coloured bead with borax of the formula .....
25. Corundum is .....
26. Gypsum is added to cement to slow down the ..... to increase strength.
27.  $\text{Be}_2\text{C}$  and  $\text{Al}_4\text{C}_3$  are called ..... because they react with  $\text{H}_2\text{O}$  yielding methane.
28.  $\text{Si}_3\text{N}_4$ ,  $\text{B}_4\text{C}$  and  $\text{SiC}$  are ..... ceramics.

## Matrix-Match Type Questions

### I. Only One Correct

1. Match the compounds (in List I) with their use (in List II).

| Compound (List I)      | Use (List II)                 |
|------------------------|-------------------------------|
| A. Boric acid          | 1. In Friedel-Craft acylation |
| B. Borax               | 2. Mild antiseptic            |
| C. Aluminium chloride  | 3. Washing powder             |
| D. Sodium peroxoborate | 4. Buffer                     |

2. Match the types of borates (in List I) with their formula (in List II).

| Types of borates (List I) | Formula (List II)                            |
|---------------------------|----------------------------------------------|
| A. Metaborate             | 1. $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ |
| B. Orthoborates           | 2. $\text{Mg}_2\text{B}_2\text{O}_5$         |
| C. Pyroborates            | 3. $\text{K}_3(\text{BO}_2)_3$               |
| D. Perborate              | 4. $\text{Ca}_3(\text{BO}_3)_2$              |

3. Match the items (in List I) with their formula (in List II).

| Items (List I)     | Formula (List II)                                               |
|--------------------|-----------------------------------------------------------------|
| A. Tetraboric acid | 1. $\text{B}_3\text{N}_3\text{H}_6$                             |
| B. Borax           | 2. $\text{Ga}(\text{OH})_2$                                     |
| C. Borazine        | 3. $\text{H}_2\text{B}_4\text{O}_7$                             |
| D. Amphoteric      | 4. $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ |

### II. One or More Correct

1. Match the compounds in Column I with their corresponding property (ies) in Column II.

| Column I            | Column II                                                                                  |
|---------------------|--------------------------------------------------------------------------------------------|
| A. Borax            | 1. Electron deficient                                                                      |
| B. Ortho boric acid | 2. $sp^2$ hybridisation                                                                    |
| C. Borane           | 3. Coloured beads with $\text{CuO}$                                                        |
| D. Alums            | 4. Mordant in dyeing                                                                       |
| E. Boron nitride    | 5. Triangular planar                                                                       |
|                     | 6. Changes $\text{CH}_3\text{CH}=\text{CH}_2$ into alcohol by anti-Markownikoff's addition |

2. Match the species in Column I with their characteristics in Column II.

| Column I              | Column II                                    |
|-----------------------|----------------------------------------------|
| A. Benzene            | 1. Six-membered ring                         |
| B. Borazine           | 2. Delocalisation of $\pi$ -electrons        |
| C. Inorganic graphite | 3. $sp^2$ -hybridised                        |
| D. Borane             | 4. Mole fraction of hydrogen 0.5             |
|                       | 5. Mole fraction of nitrogen and boron equal |
|                       | 6. Mole fraction of boron 0.25               |

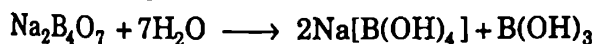
### Integer Answer Types

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the ORS have to be darkened. For example, if the correct answers to question number X, Y, Z and W (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will like the following :

| X | Y | Z | W |
|---|---|---|---|
| ① | ① | ① | ① |
| ② | ② | ② | ② |
| ③ | ③ | ③ | ③ |
| ④ | ④ | ④ | ④ |
| ⑤ | ⑤ | ⑤ | ⑤ |
| ⑥ | ⑥ | ⑥ | ⑥ |
| ⑦ | ⑦ | ⑦ | ⑦ |
| ⑧ | ⑧ | ⑧ | ⑧ |
| ⑨ | ⑨ | ⑨ | ⑨ |

### Set I

- Maximum covalency of aluminium is
- In the hydrolysis of borax



products formed are to be neutralised by HCl. Number of moles of HCl required per mole of borax hydrolysed is

- Total number of B and N atom in borazine is .....
- $\text{B}(\text{OH})_3$  can accept ..... hydroxide ion(s) from  $\text{H}_2\text{O}$ .
- Aluminium methanide contains ..... carbon atom(s).
- $\Delta G$  is negative for the following reaction



when  $x = \dots\dots\dots$

- Out of  $\text{B}_2\text{Cl}_4$ ,  $\text{GaCl}_2$ ,  $\text{GaS}$  and  $\text{S}_2$  number of diamagnetic substances are .....
- Number of tribasic acid out of the following is .....  
 $\text{H}_3\text{BO}_3$ ,  $\text{H}_3\text{PO}_3$ ,  $\text{H}_3\text{PO}_2$ ,  $\text{H}_3\text{PO}_4$

### Set II

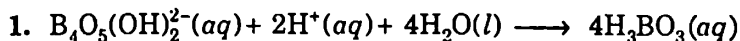
- Alum is found to contain hydrated monovalent cation, trivalent cation and sulphate in the simplest ratio  $x : y : z$  where  $x + y + z = \dots\dots\dots$
- Borax is found to have ..... tetrahedral unit(s).
- $\text{B}_2\text{H}_6$  has B—H terminal bonds and B—H bridging bonds which is equal to .....
- Total electrons involved in all the B—H bridging bond is .....
- Total electrons involved in all the B—H terminal bonds is .....
- A  $x$ -membered ring is formed in  $(\text{BN})_x$  where  $x$  is .....
- $\text{Al}(s)$  is to be converted into  $\text{Al}^{3+}(aq)$  ion. How many steps are involved? (Assume ionisation in one step)
- $\text{Cl}_2(g)$  is to be converted into  $\text{Cl}^-(aq)$  ion. How many steps are involved?

# Answers & Solutions

## Master Exercises

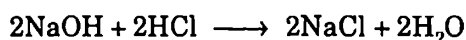
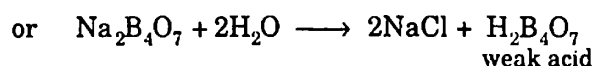
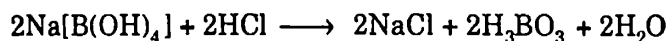
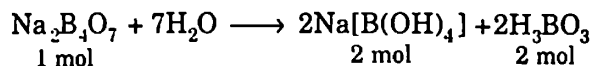
### Exercise 1

#### Short Answer Type Questions

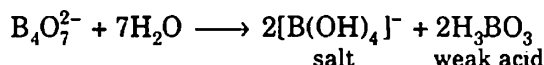


No, it does not; the mole ratio of the ion to the  $\text{H}^+$  ions is the same in both cases.

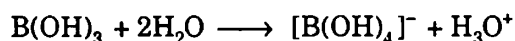
2. When borax is dissolved in water, both  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$  are formed, but only  $[\text{B}(\text{OH})_4]^-$  reacts with  $\text{HCl}$ .  $[\text{B}(\text{OH})_3]$ , called orthoboric acid, does not react with  $\text{HCl}$



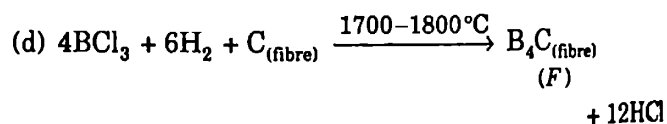
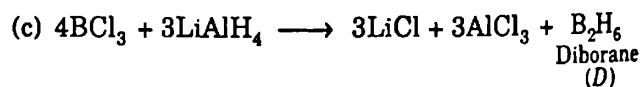
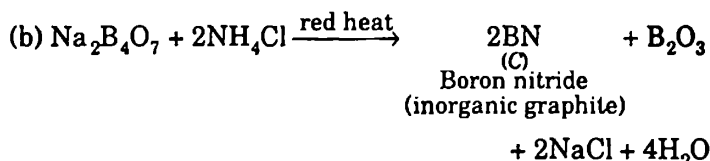
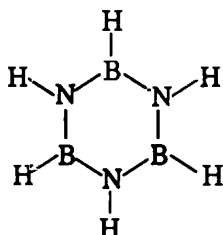
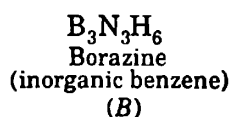
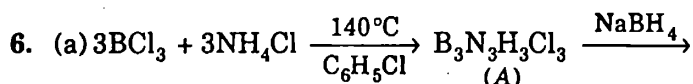
3. Borax can be used as a buffer since, its aqueous solution contains equal moles of weak acid ( $\text{H}_3\text{BO}_3$ ) and its salt  $\text{Na}[\text{B}(\text{OH})_4]$ .



4. Since,  $\text{B}(\text{OH})_3$  only partially reacts with  $\text{H}_2\text{O}$  to form  $\text{H}_3\text{O}^+$  and  $[\text{B}(\text{OH})_4]^-$ , it behaves as a weak acid. Thus, sharp end point is not obtained when it is titrated with  $\text{NaOH}$ :



5. (a)  $\text{H}_3\text{BO}_3$  (b)  $\text{B}(\text{OH})_3$  (c) it looks like a hydroxide

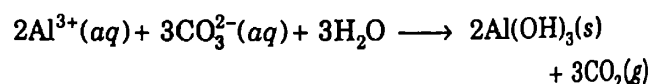


7. Bond order : bond  $X = 1$  (formed by two electrons)  
 $Y = 0.5$  (formed by one electron)

(Also see text)

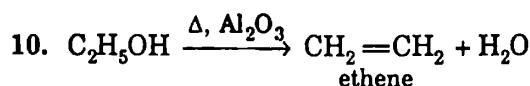
8. Refer text.

9. Fire extinguishers can be made that contain aluminium sulphate together with the usual carbonate and acid. When the extinguisher is used,  $\text{Al}(\text{OH})_3$  is produced:

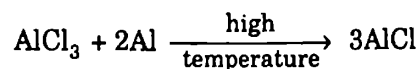


The hydroxide has the virtue of stabilising the foam, which covers the fire.

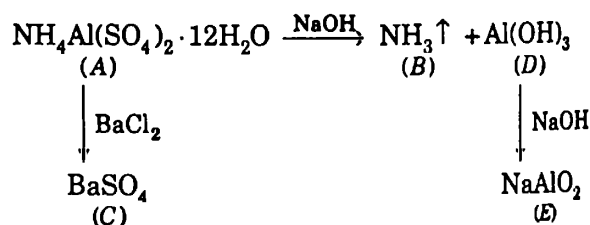
Particles of  $\text{Al}(\text{OH})_3$  are able to attach themselves to the fibres in cloth. The hydroxide is able to adsorb dye molecules much more efficiently than the fibres alone. A substance like  $\text{Al}(\text{OH})_3$  that assists in dyeing of a fabric is called a **mordant**.



11.  $\text{AlCl}_3$  forms  $\text{AlCl}$  in the gas phase at elevated temperatures:



12. (A) :  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (B) :  $\text{NH}_3$  (C) :  $\text{BaSO}_4$   
(D) :  $\text{Al}(\text{OH})_3$  (E) :  $\text{NaAlO}_2$

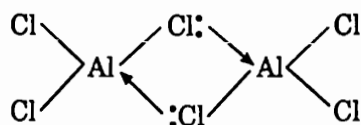


13.  $\text{Ti}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$ , etc. (of approximately same size as that of  $\text{Al}^{3+}$ ) can replace  $\text{Al}^{3+}$  in alums.

## Analytical Questions

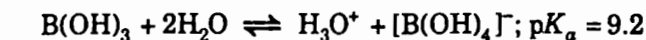
1. (i)  $\text{BCl}_3$  is stable due to stability of boron-chlorine  $\pi$ -bonding. When there is dimer formation, this bonding is disrupted as there would be no vacant orbital for  $\pi$ -bonding. It is also likely that the boron atom is too small to form the stable 4-membered ring system in such dimers.

$\text{AlCl}_3$  is electron-deficient in Al (octet-incomplete) thus behaves as Lewis acid and Al completes its octet by taking electron-pair from Cl-atom

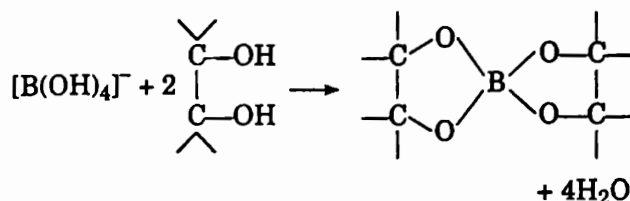


The crystalline solid has a layer-lattice with six-coordinated Al. On melting it changes to the halogen-bridged dimer  $\text{Al}_2\text{Cl}_6$  in which coordination number drops to four. This is accompanied by a dramatic increase in volume-density of the melt is nearly 45% lower than that of the solid at the melting point. The electrical conductivity also approaches zero. The dimers also dominate in gas phase.

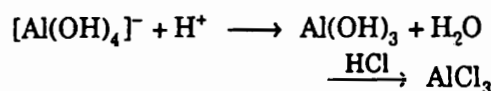
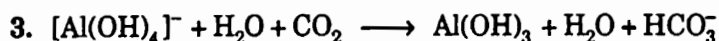
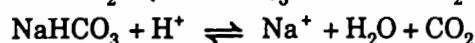
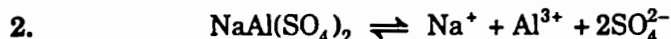
- (ii) Boron has only  $2s$ - and  $2p$ -valence orbitals and can form maximum of four bonds. Aluminium has available  $3d$ -orbitals and can use octahedral  $sp^3d^2$ -hybrid orbitals to bond to six  $\text{F}^-$  ions.
- (iii) Orthoboric acid,  $\text{H}_3\text{BO}_3$ , is soluble in water and behaves as a weak monobasic acid. It does not donate protons like most acids, but rather it accepts  $\text{OH}^-$ .



Above equilibrium can be shifted largely towards right by forming a **stable chelate** with *cis*-dihydroxy compounds (as glycol)



The proton can now be titrated against strong alkali solution using phenolphthalein indicator.



HCl converts it into  $\text{AlCl}_3$ .

4. (a), (c) and (b) : molecular

(b) : three dimensional

5. (a)  $\text{P}_4\text{O}_{10}$  (b)  $\text{B}_2\text{O}_3$  (c)  $\text{SO}_2$

6. (a) Ga (b) B (c) Tl (d) B (e) Al (f) Tl (g) B  
(h) B

## NCERT Problems

Refer Text

## Exercise 2

## Only One Option Correct

- |         |         |         |         |         |         |         |         |         |          |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|----------|
| 1. (a)  | 2. (d)  | 3. (c)  | 4. (c)  | 5. (c)  | 6. (c)  | 7. (d)  | 8. (d)  | 9. (a)  | 10. (a)  |
| 11. (d) | 12. (d) | 13. (c) | 14. (c) | 15. (c) | 16. (c) | 17. (d) | 18. (a) | 19. (d) | 20. (a)  |
| 21. (b) | 22. (a) | 23. (d) | 24. (c) | 25. (d) | 26. (a) | 27. (a) | 28. (c) | 29. (c) | 30. (a)  |
| 31. (c) | 32. (d) | 33. (a) | 34. (d) | 35. (a) | 36. (c) | 37. (d) | 38. (d) | 39. (a) | 40. (a)  |
| 41. (c) | 42. (c) | 43. (b) | 44. (d) | 45. (d) | 46. (b) | 47. (d) | 48. (d) | 49. (d) | 50. (a)  |
| 51. (a) | 52. (a) | 53. (c) | 54. (b) | 55. (c) | 56. (d) | 57. (c) | 58. (a) | 59. (d) | 60. (b)  |
| 61. (c) | 62. (d) | 63. (b) | 64. (b) | 65. (a) | 66. (c) | 67. (a) | 68. (b) | 69. (a) | 70. (c)  |
| 71. (b) | 72. (c) | 73. (c) | 74. (a) | 75. (b) | 76. (d) | 77. (b) | 78. (c) | 79. (a) | 80. (c)  |
| 81. (c) | 82. (b) | 83. (a) | 84. (d) | 85. (c) | 86. (b) | 87. (d) | 88. (c) | 89. (b) | 90. (d)  |
| 91. (c) | 92. (d) | 93. (b) | 94. (a) | 95. (d) | 96. (c) | 97. (c) | 98. (a) | 99. (d) | 100. (b) |

## One or More Than One Options Correct

1. (a,b) 2. (a,b,c,d) 3. (a,c,d) 4. (a,b,c,d)
5. (a,b,d) 6. (a,b,d) 7. (b) 8. (a,b,c) 9. (a)
10. (a,b,c,d) 11. (d) 12. (a,b,c,d)

## Passage Comprehension Questions

## Passage 1

1. (c) 2. (d)



### Passage 2

- 1. (c)      2. (a)      3. (b)      4. (d)**

### Passage 3

- 1. (b)      2. (b)      3. (a)      4. (a)**

### Passage 4

- 1. (b)      2. (b)      3. (b)      4. (d)**

### Passage 5

- 1. (a)      2. (b)**

### Assertion & Reason

1. (a)    2. (b)    3. (b)    4. (c)    5. (b)    6. (b)  
7. (a)    8. (b)    9. (b)    10. (b)    11. (b)    12. (a)  
13. (a)    14. (b)    15. (d)    16. (c)    17. (a)

## True & False

1. T    2. T    3. F    4. F    5. T    6. T  
7. T    8. T    9. F    10. T    11. F    12. T  
13. T    14. T    15. T

### Fill in the Blanks

1.  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$
2. van Arkel method
3. increases
4. inert-pair effect
5. protective layer of oxide on the surface
6. amphoteric
7. weak monobasic acid
8.  $\text{OH}^-$
9.  $sp^3$
10. paramagnetic, two unpaired
11. aluminium suboxide
12.  $\text{AlH}_3$
13. hydrolysis
14.  $\text{AlCl}_3$  and  $\text{Cl}_4$
15. high enthalpy of hydration
16.  $ns^2np^{1-6}$
17. sodium metaborate and meta-aluminate respectively
18. dimeric
19. exothermic, thermite
20. alzheimer
21. primary
22.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
23. odd
24.  $\text{Cu}(\text{BO}_2)_2$
25.  $\text{Al}_2\text{O}_3$
26. setting process
27. methanides
28. non-oxide

### Matrix-Match Type Questions

### I. Only One Correct

1. (A)—(2); (B)—(4); (C)—(1); (D)—(3)  
2. (A)—(3); (B)—(4); (C)—(2); (D)—(2)  
3. (A)—(3); (B)—(4); (C)—(1); (D)—(2)

## II. One or More Correct

1. (A)—(3); (B)—(1,2,3,5); (C)—(2,5,6); (D)—(4)  
(E)—(2)
2. (A)—(1,2,3,4); (B)—(1,2,3,4,5,6); (C)—(1,2,3,5);  
(D)—(3,6)

## Integer Answer Types

## Set I

|             |   |   |   |   |   |   |   |   |
|-------------|---|---|---|---|---|---|---|---|
| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Answers →   | 6 | 2 | 6 | 1 | 3 | 1 | 3 | 1 |
|             | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
|             | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|             | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
|             | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
|             | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
|             | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
|             | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
|             | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
|             | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
|             | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |

## Set II

|             |   |   |   |   |   |   |   |   |
|-------------|---|---|---|---|---|---|---|---|
| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Answers →   | 4 | 2 | 8 | 4 | 8 | 6 | 3 | 3 |
|             | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
|             | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|             | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
|             | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
|             | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
|             | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
|             | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
|             | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
|             | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
|             | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |

# 12

## Group 14 (IVA—The Carbon Family)

**“Carbon is a non-metal; silicon and germanium are classified as metalloids; tin and lead are metals. As a result, the elements of group 14 (Carbon family) have a broad range of chemical behaviour.”**

### Group 14 (IVA—The Carbon Family) Study of Properties

### Learning Framework of the Chapter

- Group 14 (IVA—The Carbon Family)  
Study of Properties
- Compounds of Carbon
- Compounds of Graphite
- The Carbon Cycle and Green-House Effect
- Silicon
- Compounds of Silicon
- Compounds of Tin
- Compounds of Lead

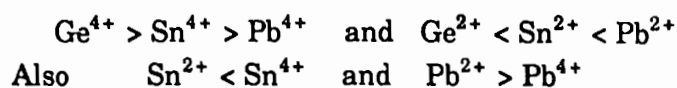
Table 12.1

| Element   | Z  | Electronic configuration | Oxidation state                  |        |
|-----------|----|--------------------------|----------------------------------|--------|
| Carbon    | C  | 6                        | [He] $2s^2 2p^2$                 | +2, +4 |
| Silicon   | Si | 14                       | [Ne] $3s^2 3p^2$                 | +4     |
| Germanium | Ge | 32                       | [Ar] $3d^{10} 4s^2 4p^2$         | +2, +4 |
| Tin       | Sn | 50                       | [Kr] $4d^{10} 5s^2 5p^2$         | +2, +4 |
| Lead      | Pb | 82                       | [Xe] $4f^{14} 5d^{10} 6s^2 6p^2$ | +2, +4 |

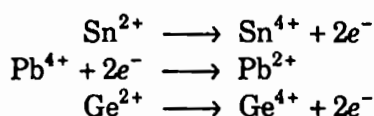
Group 14 (IVA, carbon family) has  $ns^2 np^2$  configuration of the valence shell, their most common oxidation state is +4, as in  $CCl_4$ ,  $SiCl_4$ ,  $GeCl_4$ ,  $SnCl_4$  and  $PbCl_4$ . These are volatile, molecular liquids in which atom uses tetrahedral  $sp^3$  hybrid orbitals to form covalent bonds to the Cl atoms.

Carbon is a non-metal. Silicon and germanium are metalloids and are used in semiconductors. Tin and lead are metals.

Carbon and silicon have tetravalent nature in most of the compounds when  $ns^2$  pair is also involved in bonding. Germanium, tin and lead show +2 and +4 oxidation states depending on whether  $ns^2$  pair is inert (and is not involved in bonding) or  $ns^2$  pair is involved in bonding—a case of **inert pair effect**. As we go down the group, inertness of  $ns^2$  pair increases hence tendency to exhibit +2 oxidation state increases and that of +4 oxidation state decreases. Thus, stability of



Thus,  $\Delta G^\circ < 0$  for the reactions :



Thus,  $\text{Sn}^{2+}$  salts are better reducing agents and  $\text{Pb}^{4+}$  salts are better oxidising agents. Physical properties of group 14 (IVA) are summarised in Table 12.2 and Fig. 12.1.

The +2 oxidation state occurs for tin and lead and is the most stable oxidation state for lead. Both  $\text{Sn}^{2+}(\text{aq})$  and  $\text{Pb}^{2+}(\text{aq})$  are common solution species, but there are no simple  $M^{4+}(\text{aq})$  ions for any of the group 14 (IVA) elements. Instead  $M^{4+}$  species exist in solution as covalently bonded complex ions, e.g.,  $\text{SiF}_6^{2-}$ ,  $\text{GeCl}_6^{2-}$ ,  $\text{Sn}(\text{OH})_6^{2-}$  and  $\text{Pb}(\text{OH})_6^{2-}$ . In general, the +4 oxidation state compounds are covalent, and the compounds with the Sn and Pb in the +2 oxidation state are largely ionic.

Table 12.2 Physical Properties of Carbon Family [Group 14, (IVA)]

| Property                                      | C                                                | Si                                    | Ge                    | Sn                               | Pb                           |
|-----------------------------------------------|--------------------------------------------------|---------------------------------------|-----------------------|----------------------------------|------------------------------|
| Covalent radius/(pm)                          | 77                                               | 117                                   | 122                   | 140                              | 146                          |
| Ionic radius $M(\text{IV})$ /(pm)             | —                                                | 40                                    | 53                    | 69                               | 78                           |
| $M(\text{II})$ /(pm)                          | —                                                | —                                     | 73                    | 118                              | 119                          |
| $(IE)_1$ /kJ mol <sup>-1</sup>                | 1086                                             | 786                                   | 760                   | 707                              | 715                          |
| $(IE)_2$ /kJ mol <sup>-1</sup>                | 2354                                             | 1573                                  | 1534                  | 1409                             | 1447                         |
| $(IE)_3$ /kJ mol <sup>-1</sup>                | 4622                                             | 3232                                  | 3300                  | 2943                             | 3087                         |
| $(IE)_4$ /kJ mol <sup>-1</sup>                | 6223                                             | 4351                                  | 4409                  | 3821                             | 4081                         |
| Electronegativity (Pauling)                   | 2.5                                              | 1.8                                   | 1.8                   | 1.8                              | 1.8                          |
| Melting point/°C                              | 4100                                             | 1420                                  | 945                   | 232                              | 327                          |
| Boiling point/°C                              | —                                                | 3280                                  | 2850                  | 2623                             | 1751                         |
| Electrode potential $E^\circ$                 |                                                  |                                       |                       | —                                |                              |
| $M^{2+} + 2e^- \longrightarrow M(\text{s})$   | —                                                | —                                     | —                     | -0.14V                           | -0.13V                       |
| $M^{4+} + 2e^- \longrightarrow M^{2+}$        | —                                                | —                                     | —                     | 0.15 V                           | 1.46V                        |
| Abundance in earth's crust (mass%)            | 0.020                                            | 28.2                                  | 0.0015                | 0.0002                           | 0.0013                       |
| Density (g/cm <sup>3</sup> )                  | 3.51 (diamond)                                   | 2.33                                  | 5.35                  | 7.28 (white)                     | 11.3                         |
| Occurrence                                    | Free state and combined state                    | Found in rocks as silicon or silicate | Rare element          | Found as tinstone $\text{SnO}_2$ | Found as galena $\text{PbS}$ |
| Allotropic forms                              | Crystalline (diamond and graphite) and amorphous | Crystalline and amorphous             | Two crystalline forms | White grey rhombic               | None                         |
| $M$ - $M$ bond energy (kJ mol <sup>-1</sup> ) | 348.0                                            | 297.0                                 | 260.0                 | 240                              | —                            |
| Nature                                        | Non-metal                                        | Metalloids                            | Metalloids            | Metal                            | Metal                        |

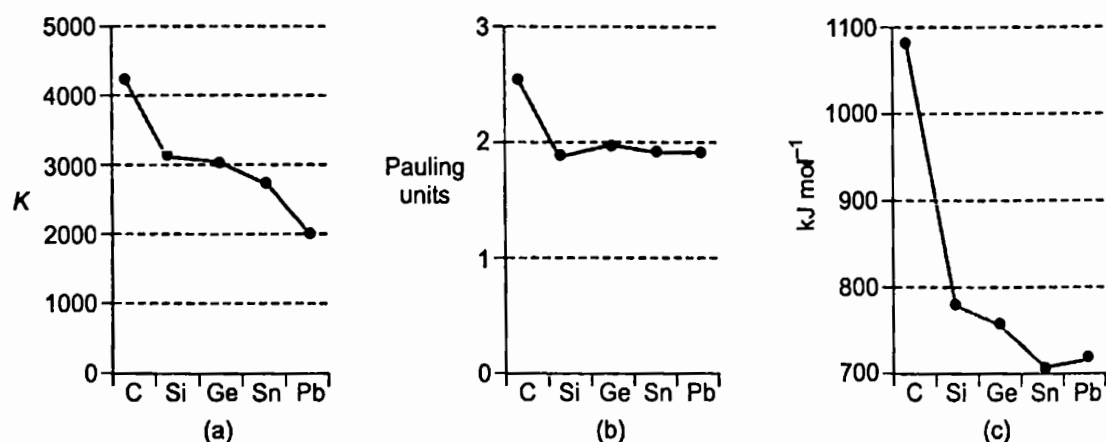


Fig. 12.1 Some group trends of the group 14 elements; (a) Boiling point, (b) Pauling electronegativity and (c) First ionisation energy.

## Occurrence

- Carbon is the **seventeenth**, (0.8%) and silicon the **second most** (27.6%) abundant element by mass in the earth's crust. Crude oil and coal are the most common forms of combined and free carbon respectively. Flakes of graphite occur in metamorphosed sedimentary rocks like quartz. Diamond occurs embedded in other rocks (as Kimberlite). Germanium is about 1-2 ppm in tin about 2.1 ppm and lead about 13-16 ppm.

|           |           |
|-----------|-----------|
| Carbon    | 0.8%      |
| Silicon   | 27.6%     |
| Germanium | 1-2 ppm   |
| Tin       | 2.1 ppm   |
| Lead      | 13-16 ppm |

### Some stable isotopes

Carbon  $^{12}\text{C}$ ,  $^{13}\text{C}$ ,  $^{14}\text{C}$

Silicon  $^{28}\text{Si}$ ,  $^{29}\text{Si}$ ,  $^{30}\text{Si}$

Germanium  $^{70}\text{Ge}$ ,  $^{72}\text{Ge}$ ,  $^{73}\text{Ge}$ ,  $^{74}\text{Ge}$ ,  $^{76}\text{Ge}$

Tin Ten stable isotopes of mass numbers :  
112, 114, 115, 116, 118, 119, 120, 122, 124

Lead  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$

## Ionisation Energy

The ionisation energies (Table 12.2 indicate that a very large amount of energy is required to form a  $M^{4+}$  ion, therefore, not many ionic compounds are formed by group 14 elements in the +4 oxidation state. On the other hand, the promotion of one of the  $ns$  electrons to the  $np$  vacant orbital, as shown below, can allow a tetravalency. In fact, most of the tetravalent compounds formed by elements of this group are covalent in nature. Electronic configuration of carbon in the ground and excited state is given as an example.

Electronic configuration of C in ground state

| 1s                   | 2s                   | 2p                 |
|----------------------|----------------------|--------------------|
| $\uparrow\downarrow$ | $\uparrow\downarrow$ | $\uparrow\uparrow$ |

C in excited state

| 1s                   | 2s         | 2p                         |
|----------------------|------------|----------------------------|
| $\uparrow\downarrow$ | $\uparrow$ | $\uparrow\uparrow\uparrow$ |

Four unpaired electrons can form four equivalent covalent bonds — a case of  $sp^3$  hybridisation.

### DEEP Focus

Since, the sum of the first two ionisation energies also decreases down the group, it becomes increasingly favourable thermodynamically, for Sn and Pb to form compounds in oxidation state +2 which are more ionic in character.

If we go through the data for ionisation energies given in Table 12.2, we find that the first and second ionisation energies decrease down the group from C to Sn as expected, but they increase slightly when we move to Pb.

On the other hand, both the 3rd and the 4th ionisation energies vary irregularly, their sequence is  $\text{C} > \text{Ge} > \text{Si} > \text{Pb} > \text{Sn}$ .

The decrease in the 1st and 2nd ionisation energies from C to Sn is because of the increase in atomic size down the group. The 3rd and 4th ionisation energies increases from Si to Ge because of poor shielding of 4s-electrons offered by the 3d-electrons against the increased nuclear charge in Ge. All the ionisation energies are slightly higher in case of Pb. This increase can again be attributed to the poor shielding effect of the 4f and 5d orbital electrons. Further, the s-electrons being more penetrating, experience higher nuclear charge which makes it difficult to remove them.

- On account of high ionisation energies, simple  $M^{4+}$  ions of the group are not known.
- The tendency to form negative ions by gaining electrons is only in carbon. For C and Si, stable divalent compounds  $\text{MX}_2$  are very rare.

## Size

The covalent radii of the elements, as expected, increase with increase in atomic number. This increase, however, is not uniform. When we move from carbon to silicon the covalent radius increases sharply, and then increases in gradual.

## Explanation

A large increase in the size of silicon is due to the introduction of the 3rd shell. When we go down to germanium, the 4th shell is introduced, no doubt, but the effective nuclear charge resulting from addition of eighteen protons to the nucleus out balances the effect of the additional shell leading to only a marginal increase in size. Similarly, in case of Pb, the increase in covalent radius is very small in comparison to that in Sn. This is further reflected in the ionisation energies and electron affinities of these elements.

## Electronegativity

Carbon has higher electronegativity as compared to other elements of the group. As a result, it can accept (gain) electrons and can form negative ions of the kind  $\text{C}_2^{2-}$  in acetylides and  $\text{C}^{4-}$  in methanides, while the other elements in the group are unable to do so. When we see the electronegativity trends in the group, we find that the value decreases down the group as expected, with Ge as an exception whose electronegativity is slightly higher than that of Si. As explained above, this could be due to the higher effective nuclear charge in case of Ge.

## Catenation

Catenation is a property by virtue of which elements form long chain compounds by single or multiple bond formation between atoms of the same element. Carbon shows this tendency to a remarkable extent because of its small size and high bond energy (Table 12.2), Si and Ge to

a lesser extent and Sn and Pb to a very small extent. In case of carbon we have alkanes, *e.g.*, ethane propane butane, pentane, etc. These are chains of carbon hydrides having the general formula  $C_nH_{2n+2}$ , where  $n$  can be a large number, alkanes with  $n=100$  are known. Carbon also forms a number of catenated halides, *e.g.*, polyvinyl chloride (PVC). Silicon forms silanes having the general formula  $Si_nH_{2n+2}$ , but  $n$  does not exceed 8. Its halides also shows catenation and have a general formula  $Si_nX_{2n+2}$ , where if  $X = F$ ,  $n = 1$  to 14; if  $X = Cl, Br$  or  $I$ ,  $n = 1$  to 10. Germanium forms germanes, with general formula  $Ge_nH_{2n+2}$ , where  $n = 1$  to 9. Germanium halides form dimers, *e.g.*,  $Ge_2Cl_6$ . Hydrides of Sn and Pb are much less stable, while  $SnH_4$  and  $Sn_2H_6$  have been prepared, analogous methods fail for the preparation of  $PbH_4$ . No catenated halides are known for Sn and Pb.

- There is steady decrease in the  $M-M$  bond energy as we go down the group.

## Multiple Bonding

In group 14, carbon is the only element capable of forming comparatively stable multiple bonds with another C atom and also with N, O, etc. Examples are alkenes ( $>C=C<$ ), alkynes ( $-C\equiv C-$ ), imines ( $>C=N-$ ), nitriles ( $-C\equiv N$ ), ketones ( $>C=O$ ), etc. None of the other elements of the group forms stable compounds containing multiple bonds. Recently, some success has been achieved in synthesising compounds with  $>Si=Si<$  and  $>Si=C<$  double bonds. Stoichiometric analogues like  $SiO_2$ ,  $SnO_2$  are  $(Me_2SiO)_n$  are known which are giant macromolecules containing  $M-O-M$  linkages.

The tendency of formation of multiple bonds easily, in case of carbon, is because of the high bond energy (Table 12.3) and a small atomic radius of carbon as compared to other elements of the group. So its  $p$ -orbitals can approach the  $p$ -orbitals of the other C, O or N atom for an effective overlap essential for  $\pi$ -bond formation.



Table 12.3 Bond Energies of Group 14 Elements ( $\text{kJ mol}^{-1}$ )

| Bond        | C   | Si  | Ge  | Sn  | Pb |
|-------------|-----|-----|-----|-----|----|
| $E-E$       | 347 | 226 | 118 | 150 | —  |
| $E=E$       | 611 | 318 | —   | —   | —  |
| $E\equiv E$ | 837 | —   | —   | —   | —  |
| $E-H$       | 414 | 318 | 285 | 251 | —  |
| $E-O$       | 360 | 464 | 360 | —   | —  |
| $E=O$       | 736 | 640 | —   | —   | —  |

$E^*$  = Element C, Si, Ge, Sn or Pb.

## Allotropes

- Carbon and graphite are two allotropes of carbon. In diamond (Fig. 12.2(a)) each carbon atom is linked tetrahedrally to four, other carbon atoms by  $sp^3$  bonds and a giant covalent network is formed. It is,

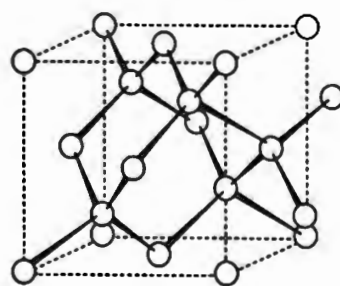
therefore, hard and non-conducting. Graphite (Fig. 12.2(b) and (c)) is more thermodynamically stable allotrope.

## DEEP Focus

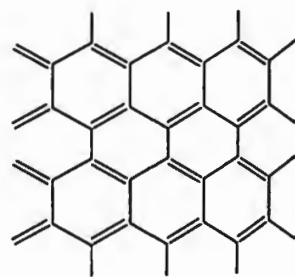
Graphite consists of planar hexagonal layers of carbon atoms held together by relatively weak van der Waals' forces. Within each layer, a carbon atom is bonded to three other carbon atoms by  $sp^2$  hybrid bonds and the additional  $p$  electron from each carbon forms an extended delocalised  $\pi$ -bonding system encompassing the entire layer. This makes graphite a good conductor of electricity in directions along the planes of carbon atoms. The covalent bonds in graphite account for its hardness; however, because the layers can slide over one another, graphite is slippery to touch and is effective as a lubricant.

Silicon exists only in the diamond structure due to tendency to form  $p\pi-p\pi$  bonds to itself. Fullerene, [Fig. 12.2(d)] a carbon allotrope discovered in 1990 as a constituent of soot, consists of spherical  $C_{60}$  molecules with the extraordinary shape of a soccer ball. The  $C_{60}$  ball has 12 pentagonal and 20 hexagonal faces with each atom  $sp^2$ -hybridised and bonded to three other atoms.

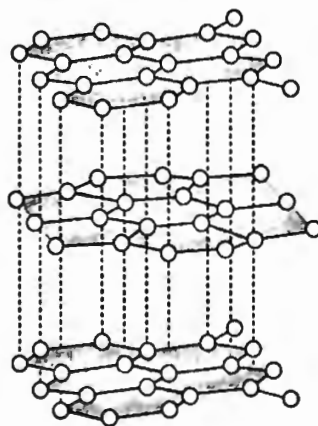
$C_{60}$  was first prepared in 1985, by laser vaporisation of graphite (at about  $10000^\circ\text{C}$ ) followed by sweeping of the carbon atoms by sweeping of the carbon atoms by a blast of high pressure helium gas and rapid cooling in a vacuum chamber (Richard Smaller, Rice university Texas and Harry Kroto, University of Sussex, U.K. Noble Prize Winners (1990).)



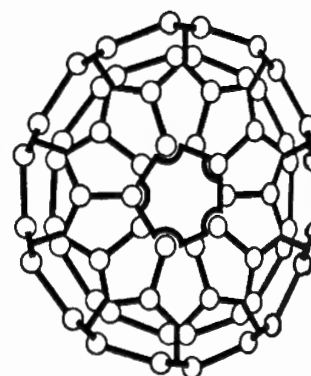
(a) The crystal structure of diamond



(b) The structure of a graphite sheet



(c) Structure of  $\alpha$ -graphite

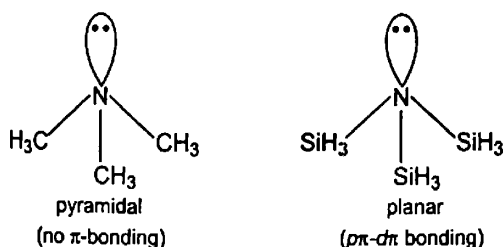


(d) Structure of Buckminster fullerene

Fig. 12.2 Allotropes carbon

### DEEP Focus

- Silicon also uses  $d$ -orbitals in multiple bonding, In case of  $N(CH_3)_3$ , geometry is pyramidal, but in case of  $N(SiH_3)_3$  it is planar. It is due to the fact that in the latter, the lone pair of N-atom is transferred to the empty  $d$ -orbitals of silicon ( $p\pi-d\pi$  overlapping) :



- The normal valency of the elements is four, but apart from carbon, the elements can make more than four bonds. This is because they make use of a set of  $d$ -orbitals in bonding. Thus availability of  $d$ -orbitals (empty but electrons of  $ns^2$  and  $np^2$  can be excited into this) is responsible for the ability of the elements, except carbon, to make complex ions such as  $SiF_6^{2-}$  (Fig. 12.3).

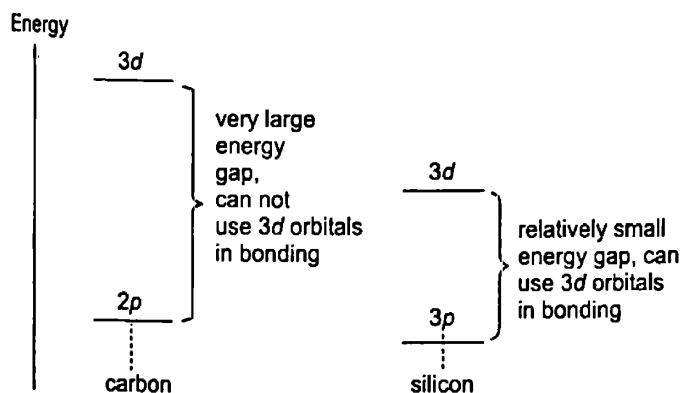
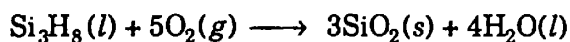


Fig. 12.3 Energy difference between  $2p$  and  $3d$  energy levels in carbon and between  $3p$  and  $3d$  energy levels in silicon

- The main chemical differences between silicon and carbon are
  - Si does not form stable double bonds,
  - Si does not form very stable Si—Si bonds,
  - Si has vacant  $3d$ -orbitals in its valence shell into which it can accept electrons from donor atoms.
- Some carbon compounds are less reactive than the corresponding compounds of the other members of the group.  $CCl_4$  has no interaction with  $H_2O$  (hydrolysis) whereas  $SiCl_4$  does by use of empty  $3d$ -orbitals.
- All the elements give hydrides. Carbon, of course gives an immense number, but silicon and germanium also show a wide variety.

|         |                  |
|---------|------------------|
| $CH_4$  | methane (alkane) |
| $SiH_4$ | stannate         |
| $GeH_4$ | germane          |
| $SnH_4$ | stannane         |
| $PbH_4$ | plumbane         |

Carbon hydrides will not ignite in air unless a flame is put to them. Apart from silane,  $SiH_4$ , the silicon hydrides are less well behaved.  $Si_3H_8$  is spontaneously flammable in air :



Alkane as well as silane are not hydrolysed however, traces of alkali converts silane into hydrated silica  $SiO_2 \cdot nH_2O$ .

- As we descend the group, acidic nature of the oxides decreases and basic nature of the oxides increases.

| Oxides       | Nature     | Oxides       | Nature     |
|--------------|------------|--------------|------------|
| $CO, CO_2$   | acidic     | $SnO, SnO_2$ | amphoteric |
| $SiO_2$      | acidic     | $PbO, PbO_2$ | basic      |
| $GeO, GeO_2$ | amphoteric | $Pb_3O_4$    | amphoteric |

Si, Ge, Sn and Pb form oxides  $MO_2$ .  $SiO_2$  is an infinite three-dimensional network solid of silicon and oxygen atoms connected by single covalent bonds.  $GeO_2, SnO_2$  and  $PbO_2$  are all solids and exist in several modifications.

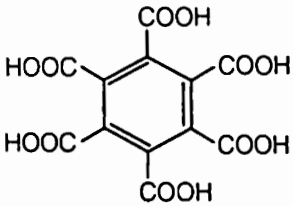
**Illustration 1** Why is graphite a better electrical conductor than diamond and why does the conductivity of graphite depend on direction?

**Solution** Graphite has a two-dimensional sheet like structure in which each carbon atom uses  $sp^2$  hybrid orbitals to form trigonal planar  $\sigma$  bonds to three neighbouring carbon atoms. In addition, each carbon atom uses its remaining  $p$ -orbital, perpendicular to the plane of the sheet, to form a  $\pi$  bond. Because each carbon atom must share its  $\pi$  bond with its three neighbours, the  $\pi$  electrons are delocalised and are free to move in the plane of the sheet. As a result, the electrical conductivity of graphite in a direction parallel to the sheet is about  $10^{20}$  times greater than the conductivity of diamond. The conductivity of graphite perpendicular to the sheets of carbon atoms is lower because electrons must hop from one sheet to the next. The substance or crystal that show different properties in different directions is called **Anisotropic**.

### Chemical Reactivity

Elements in this group are relatively unreactive, but reactivity increases down the group. Lead often appears more noble (unreactive) than expected. It is due to a surface coating of oxide and partly due to high overpotential for the reduction of  $H^+$  to  $H_2$  at a lead surface. The production of  $H_2$  from  $H^+$  at a lead electrode is kinetically unfavourable, hence a much larger potential is required than the standard reduction potential. Table 12.4 summarises reactions of the elements with different reagents :

Table 12.4 Reactivity of the Elements of Group 14 (IVA)

| Reagent            | Reactivity                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |
|--------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| H <sub>2</sub> O   | <ul style="list-style-type: none"> <li>• C, S, Ge unaffected by H<sub>2</sub>O.</li> <li>• Sn reacts with steam forming SnO<sub>2</sub> and H<sub>2</sub> :<br/> <math display="block">\text{Sn} + 2\text{H}_2\text{O} \xrightarrow{\text{(steam)}} \text{SnO}_2 + 2\text{H}_2</math> </li> <li>• Pb is unaffected by H<sub>2</sub>O probably because of protective oxide film.</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |
| Dilute acids       | <ul style="list-style-type: none"> <li>• C, Si, Ge unaffected by dilute acid.</li> <li>• Sn dissolves in dilute HNO<sub>3</sub> forming Sn(NO<sub>3</sub>)<sub>2</sub>.</li> <li>• Pb dissolves slowly in dilute HCl forming PbCl<sub>2</sub> (sparingly soluble) and quite readily in dilute HNO<sub>3</sub> forming Pb(NO<sub>3</sub>)<sub>2</sub> and oxides of nitrogen.</li> <li>• Pb does not dissolve in dilute H<sub>2</sub>SO<sub>4</sub> due to formation of PbSO<sub>4</sub> coating.</li> </ul>                                                                                                                                                                                                                                                                                                                                                                              |
| Concentrated acids | <ul style="list-style-type: none"> <li>• Diamond is unaffected by concentrated acids, but graphite changes to mellitic acid (C<sub>12</sub>H<sub>6</sub>O<sub>12</sub>) also called benzene hexa-carboxylic acid (A)</li> </ul> <div style="text-align: center;"> <p>A:</p>  </div> <ul style="list-style-type: none"> <li>with hot concentrated HNO<sub>3</sub> and to graphite oxide with hot concentrated HF/HNO<sub>3</sub>.</li> <li>• Si is oxidised and changes to SiF<sub>4</sub> by hot concentrated HNO<sub>3</sub>/HF.</li> <li>• Ge dissolves slowly in hot concentrated H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>.</li> <li>• Sn also dissolves in concentrated acids.</li> <li>• Pb does not dissolve in concentrated HCl due to formation of PbCl<sub>2</sub> coating.</li> </ul> |
| Alkalies           | <ul style="list-style-type: none"> <li>• Carbon is unaffected by alkalies.</li> <li>• Si reacts slowly with cold aqueous NaOH solution, and readily with hot solution forming SiO<sub>4</sub><sup>4-</sup>.</li> <li>• Sn and Pb are slowly attacked by cold alkali, and rapidly by hot alkali, giving stannates Na<sub>2</sub>[Sn(OH)<sub>6</sub>] and plumbates Na<sub>2</sub>[Pb(OH)<sub>6</sub>].</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
| Halogens           | <ul style="list-style-type: none"> <li>• Diamond is unreactive, but graphite reacts forming (CF)<sub>n</sub>.</li> <li>• Si and Ge form volatile SiX<sub>4</sub> and GeX<sub>4</sub>.</li> <li>• Sn and Pb are less reactive. Sn reacts with Cl<sub>2</sub> and Br<sub>2</sub> in cold, and with F<sub>2</sub> and I<sub>2</sub> on warming. Lead reacts with F<sub>2</sub> in cold and with Cl<sub>2</sub> on heating forming PbX<sub>2</sub>.</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                               |
| Air                | <ul style="list-style-type: none"> <li>• Graphite burns above 700°C (CO) Diamond burn above 900°C (CO). Si, Ge, Sn, burn on strong heating (At 1400°C, Si also forms SiN and Si<sub>3</sub>N<sub>4</sub>) Finely divided lead powder is pyrophoric (combines highly exothermically with oxygen) but the surface is practically inactivated by a thin protective layer of oxide, chloride, sulphate. PbO is formed above 600°C.</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                |

## Uses

1. Diamonds are used in jewellery on account of their high refractive and dispersive power. Due to their exceptionally hard nature, inferior quality diamonds are used for industrial purposes mainly in the form of grit and powder in cutting, drilling, grinding and polishing tools.

Graphite electrodes are used in the extraction of aluminium. Graphite is also used for making crucibles, as a lubricant in heavy machines and as pencil lead, etc. Very pure graphite is used as a neutron moderator in nuclear reactors.

Coke is mainly used in metallurgy. Carbon black is used to strengthen rubber, as a pigment in inks, paints, paper and plastics. Activated carbon has enormous surface area and is used extensively in sugar industry as a decolourising agent. It is a very efficient adsorbent it absorbs organic pollutants from drinking water, noxious gases from the air. It is also used in the treatment of sewage water and as a catalyst. Amongst the compounds of carbon, CO<sub>2</sub> finds an important use as a fire extinguisher and in refrigeration as dry ice.

2. Silicon finds uses in both elemental and combined forms. Very pure silicon is used in making semiconductors and in solar cells which are becoming increasingly important. Silicon becomes *p*-type semiconductor when doped with a group 13 (Al, Ga) and an *n*-type semiconductor when doped with group 15 (P, As) Hyperfine Si is one of the purest materials used in the production of transistors.

Silicates are used in glass and cement manufacture.

Silicones are also widely used in lubricants. Their inert nature makes them ideal for use in gas chromatography, *e.g.*, methylphenyl silicones. Germanium is used largely in transistor technology. However, its use in optics is growing; germanium is transparent in infrared region and is, therefore, used in infrared windows, prisms and lenses.

- Silicon is extensively used in steel making as a deoxidiser. Ferrosilicon is the usual form. Steels with high Si content are corrosion resistant.
3. Due to its resistance to corrosion, tin is used to coat mild steel plate. Tinning of copper and brass utensils has been an age old practice in India. Tin is also used for making various alloys (Refer Appendix) like bronze, pewter, gun metal, etc. Tin-lead alloys are fusible and low melting. Solders, which are low melting alloys, are used to join pieces of metal together. Soldering is a very common practice for joining components of an integrated circuit. Sn—Pb alloys are also used as bearing metal or type metal.



Lead is used as an inert material, *e.g.*, for building roofs, and for cable sheathing. Lead gets covered with a layer of  $\text{PbSO}_4$ , which is insoluble and does not get attacked by common reagents. Lead pipes were used in municipal water supply at one time. Soft water, however, tends to dissolve lead and may cause lead poisoning. Therefore, galvanised iron (GI) pipes are now used for water supply.

Due to their low chemical reactivity, lead coated chambers are used in many industrial preparations like that of sulphuric acid. In view of its high density, lead is also used in making shielding blocks for radioactivity experiments. Organolead compounds, *e.g.*, tetraethyllead,  $\text{Et}_4\text{Pb}$  and tetramethyllead,  $\text{Me}_4\text{Pb}$ , are used as anti-knock additives to petrol for internal combustion engines. However, in recent times, because of their polluting nature, many countries have reduced or altogether stopped their use.

One of the major uses of lead still is in the storage batteries. Storage batteries also called lead-acid batteries have a supporting grid of lead-tin alloy (91:9) with  $\text{PbO}_2$  as the oxidising agent and spongy Pb as the reducing agent. The electrolyte is dilute  $\text{H}_2\text{SO}_4$ .

Following table summarises uses of elements of group 14 (IVA):

| Elements  | Uses                                                                                                  |
|-----------|-------------------------------------------------------------------------------------------------------|
| Carbon    | Diamond in jewellery and glass cutter, graphite as lubricant and electrode                            |
| Silicon   | As a semiconductor, in silicone waxes and polymers, as silicates in the ceramic and glass industries. |
| Germanium | As a semiconductor.                                                                                   |
| Tin       | In alloys, as a protective coating for iron and steel.                                                |
| Lead      | In alloys, in car batteries.                                                                          |

## Compounds of Carbon

Carbon is unique in the variety and complexity of compounds that it can form. The molecules that are responsible for the growth and development of living organisms, such as vitamins, proteins, enzymes, hormones and DNA, are structures built from chains of carbon.

## Oxides of Carbon

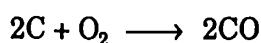
- In oxides of carbon there are  $\pi\text{--}\pi$  multiple bonds between carbon and oxygen.

stable oxides :  $\text{CO}$  and  $\text{CO}_2$

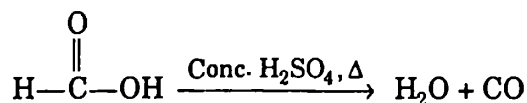
less stable :  $\text{C}_3\text{O}_2$  (carbon suboxide),  $\text{C}_5\text{O}_2$ ,  $\text{C}_{12}\text{O}_9$

least stable :  $\text{C}_2\text{O}$  (graphite oxide),  $\text{C}_2\text{O}_3$

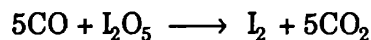
- $\text{CO}$  is a colourless, odourless, poisonous gas. It is formed when carbon is burnt in limited supply of air.



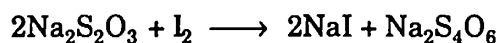
Dehydration of formic acid with conc.  $\text{H}_2\text{SO}_4$  gives  $\text{CO}$  (laboratory method).



- $\text{CO}$  can be detected because it burns with a blue flame.
- $\text{CO}$  reduces  $\text{I}_2\text{O}_5$  to  $\text{I}_2$



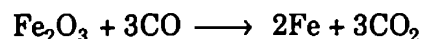
$\text{I}_2$  thus liberated is determined by titration with  $\text{Na}_2\text{S}_2\text{O}_3$  (hypo)



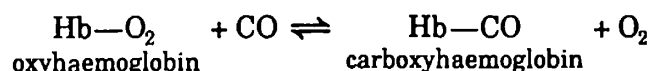
This is a quantitative method of estimation of  $\text{CO}$ .  $\text{PdCl}_2$  is also reduced to  $\text{Pd}$



Following reduction takes place in blast furnace :



- $\text{CO}$  is toxic because it forms a complex with haemoglobin in the blood, and this complex is more stable than oxy-haemoglobin. This prevents the haemoglobin in the red blood corpuscles from carrying oxygen round the body. This causes an oxygen deficiency, leading to unconsciousness and then death. The blood of victims of carbon monoxide poisoning is a brilliant red-pink colour rather than the dull red of normal blood.



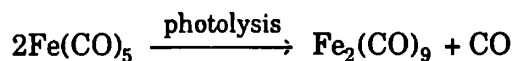
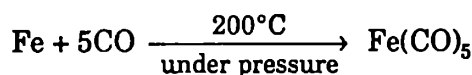
- Although  $\text{CO}$  has no acidic or basic properties (in terms of proton  $\text{H}^+$ ), it can behave as a **Lewis base—electron-pair donor**, and thus forms complexes with transition metals (mostly with zero oxidation state) :



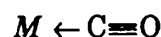
These are called carbonyl compounds and can be made by :



This is **Mond** process of the purification of Ni metal.



- Bond order between C and O is three and metal carbonyl bond is dative



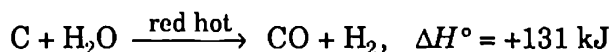
- $\text{CO}$  is sparingly soluble in water and is neutral oxide.
- $\text{CO}$  is an important fuel



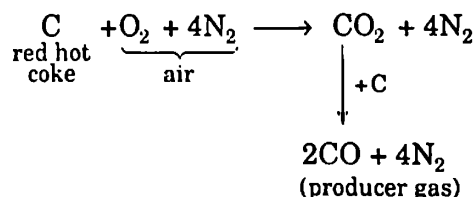


It is associated with following fuels :

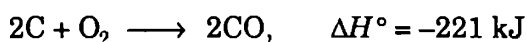
**Water gas :** Equimolecular mixture of CO and H<sub>2</sub>



**Producer gas :** A mixture of CO and N<sub>2</sub>



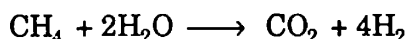
Producer gas is less efficient than water gas as only part of the gas will burn. The overall reaction is exothermic :



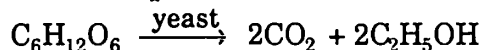
**Coal gas :** A mixture of CO, H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>.

|              |                                                        |
|--------------|--------------------------------------------------------|
| Water gas    | Co, H <sub>2</sub>                                     |
| Producer gas | Co, N <sub>2</sub>                                     |
| Coal gas     | Co, H <sub>2</sub> , CH <sub>4</sub> , CO <sub>2</sub> |

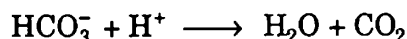
- $\text{CO} + \text{S} \longrightarrow \text{COS}$  (carbonyl sulphide)  
 $\text{CO} + \text{Cl}_2 \longrightarrow \text{COCl}_2$  (carbonyl chloride)
- CO<sub>2</sub> is a colourless and odourless gas and is generally recovered as by-product from  
 — the **manufacture of H<sub>2</sub>**



— the **fermentation processes in breweries**

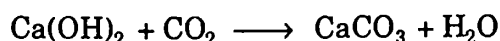


- CO<sub>2</sub> gas can be liquefied under pressure between -57°C and +31°C. Solid CO<sub>2</sub> called 'dry ice' sublimes directly to the vapour state (without going through the liquid state) at -78°C under atmospheric pressure. Dry ice (also called **cardice**) is used to freeze meat, frozen foods and ice cream, and in the laboratory as a coolant.
- CO<sub>2</sub> is used in many fire extinguishers:
  - Water based extinguishers have a sealed bottle of acid immersed in a solution of HCO<sub>3</sub><sup>-</sup> (say NaHCO<sub>3</sub>). When the extinguisher is struck, the bottle bursts, and reaction between acid and HCO<sub>3</sub><sup>-</sup> produces CO<sub>2</sub> instantly in the form of watery spray (or in a foam if other chemicals have been added).



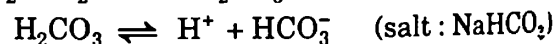
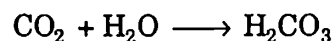
- Other extinguishers use pure CO<sub>2</sub> under pressure. The gas given out covers the fire and prevents oxygen in the air from reacting with hot materials.

- CO<sub>2</sub> is an acidic oxide and reacts with bases, forming salts:

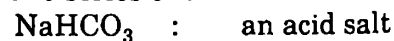


Solution of CO<sub>2</sub> in water behaves as weak dibasic acid, the solubility in water increases remarkably under

pressure. This property is used to carbonate drinks (Coca-Cola etc.)



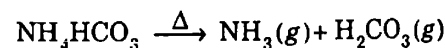
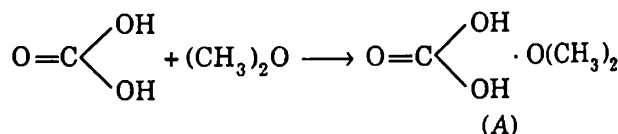
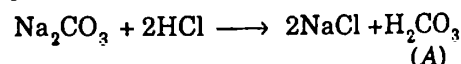
and thus forms two series of salt.



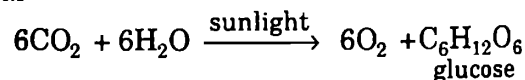
A hydrate CO<sub>2</sub> · 8H<sub>2</sub>O can be crystallised at 0°C under a pressure of 50 atm CO<sub>2</sub>.

## DEEP Focus

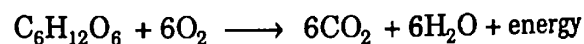
- Free carbonic acid has not been isolated but its acid salt (NaHCO<sub>3</sub>) and normal salt (Na<sub>2</sub>CO<sub>3</sub>) have been isolated. An etherate (A) of probable composition OC(OH)<sub>2</sub> · O(CH<sub>3</sub>)<sub>2</sub> is obtained by reacting Na<sub>2</sub>CO<sub>3</sub> with HCl in presence of dimethyl ether at very low temperature (-50°C). The white crystalline solid decomposes at 5°C. H<sub>2</sub>CO<sub>3</sub> is believed to be present in the gaseous phase by thermal decomposition of NH<sub>4</sub>HCO<sub>3</sub>



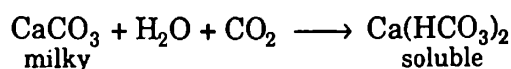
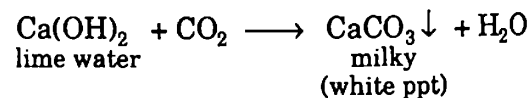
- Biologically, CO<sub>2</sub> is important in photosynthesis where the green parts of plants manufacture glucose sugar



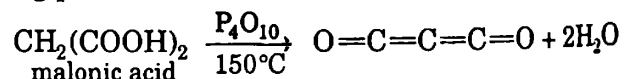
The reverse reaction occurs during the process of respiration, where animals and plants release energy :



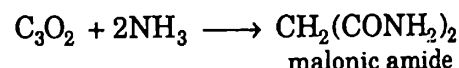
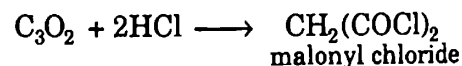
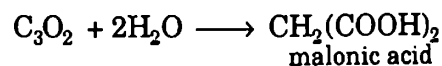
- CO<sub>2</sub> turns lime water milky which changes to colourless on passing excess of CO<sub>2</sub> in it

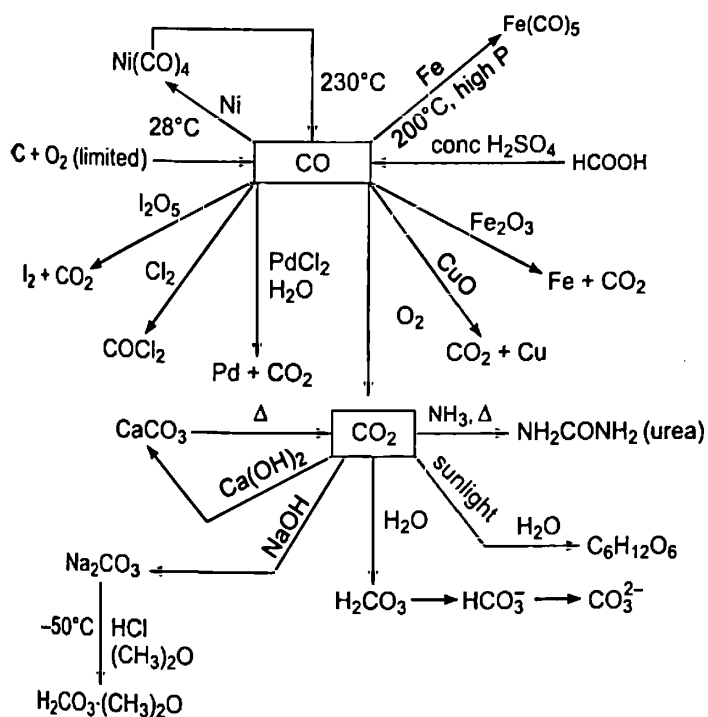


- Carbon suboxide C<sub>3</sub>O<sub>2</sub> is a foul smelling gas with boiling point 6°C.



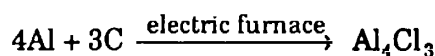
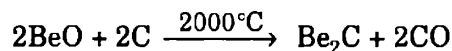
linear molecule stable at -78°C.



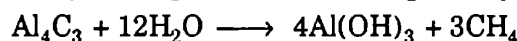
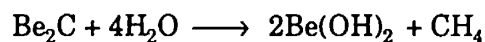


## Carbides

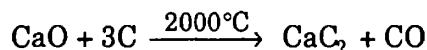
- Solid compounds of carbon with elements other than hydrogen are generally called **carbides**.
- **Ionic or salt-like carbides** are formed by the most electropositive metals such as alkali and alkaline earth metals and aluminium:



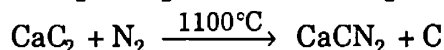
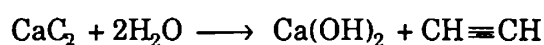
Both  $\text{Be}_2\text{C}$  and  $\text{Al}_4\text{C}_3$  are called **methanides** because they react with  $\text{H}_2\text{O}$  yielding methane:



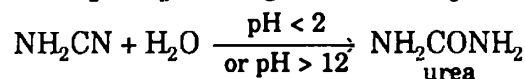
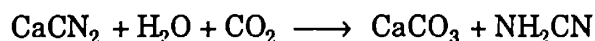
$\text{CaC}_2$  (calcium acetylide) is obtained by strongly heating lime and coke:



It is used to manufacture acetylene and calcium cyanamide:



Calcium cyanamide,  $\text{Ca}(\text{NCN})$ , is used as nitrogenous fertiliser, and to make urea:



The cyanamide ion  $[\text{N}=\text{C}=\text{N}]^{2-}$  is isoelectronic with  $\text{CO}_2$  and has the same linear structure.

$\text{C}^{2-}$  (acetylide) has multiple bonding of the type  $\text{C}\equiv\text{C}^{2-}$

while  $\text{CaC}_2$  has NaCl type of lattice with  $\text{Ca}^{2+}$  replacing  $\text{Na}^+$  and  $\text{C}_2^{2-}$  replacing  $\text{Cl}^-$ .

$\text{Mg}_2\text{C}_3$  has  $(\text{C}\equiv\text{C}-\text{C}^{3-})$  ion and gives propyne on reaction with  $\text{H}_2\text{O}$ .



- **Interstitial carbides** are formed by transition metals in which carbon atoms occupy tetrahedral holes in the close-packed arrays of metal atoms. These are generally very hard, electrically conducting and have very high melting points (tungsten carbide (WC)). Carbides of Cr, Mn, Fe, Co and Ni are hydrolysed by water or dilute acids.

- **Covalent carbides** are formed by metalloids like Si and B.  $\text{SiC}$  and  $\text{B}_4\text{C}$  (and more correctly as  $\text{B}_{10}\text{C}_2$ ) are extremely hard, infusible and chemically inert.  $\text{SiC}$  has a diamond like structure (hence also called **artificial diamond**) in which C and Si atoms are each tetrahedrally surrounded by four of the other kind of atoms under the name **carborundum**, it is used in cutting tools and abrasives. It is produced by

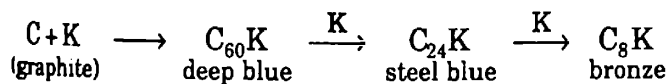
## Compounds of Graphite

### Type I : Electrically Conducting Compounds

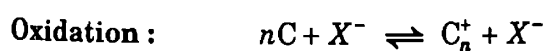
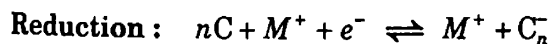
Compounds in which the  $\pi$ -electron system of graphite is retained and thus electrical conductivity is retained due to mobile electrons (or even many increase). In such compounds separation between layers increases by as much as  $10\text{\AA}$ . Such compounds are called **Lamellar compounds**.

### Preparation

- (i) Such Lamellar compounds are formed by insertion of various atoms (as alkali metals), molecules or ions (as  $\text{FeCl}_3$ ) between the graphite layers.



- (ii) By electrochemical method

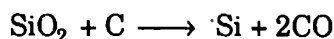


The high electrical conductivity may arise from transfer of electron(s) from the metal to the  $\pi$ -orbitals of the carbon plane, where they are free to move under an electric field.

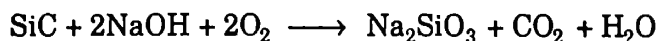
### Type II : Electrically non-conducting Compounds

Graphite changes to  $(\text{CF})_n$  — a white compound when it is treated with  $\text{F}_2$  at  $400\text{--}600^\circ\text{C}$ . It is found by X-ray study that in  $(\text{CF})_n$  layers separation is about  $6.6\text{\AA}$ . Also carbon atoms in the layers have  $sp^3$  hybridisation with boat or chair conformation and  $(\text{C}-\text{F})$  covalent bond exists. Due to loss of  $\pi$ -electron, compound  $(\text{CF})_n$  is non-conducting.

heating quartz or sand with an excess of coke in an electric arc furnace at 2000–2500°C.



SiC reacts with NaOH in presence of air and with  $\text{Cl}_2$  at 100°C.

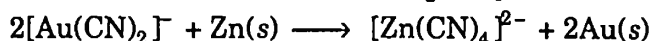
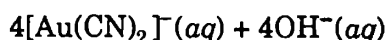
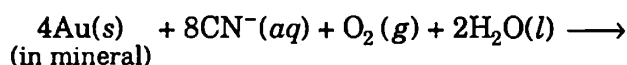


Boron carbide is even harder than silicon carbide and is used both as an abrasive and as a shield from radiation.

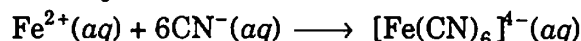
- $\text{Be}_2\text{C}$  — red solid
- $\text{Al}_4\text{C}_3$  — pale yellow solid
- $\text{CaC}_2$  — colourless
- $\text{SiC}$  — pale yellow (pure)

## Cyanides

- The cyanides contains the anion group  $:\text{C}\equiv\text{N}:^-$ . The cyanide ions are extremely toxic because they bind almost irreversibly to the Fe(III) ion in cytochrome oxidase, a key enzyme in metabolic processes involved in the oxidation of food molecules. With  $\text{CN}^-$  attached to the iron, the enzyme is unable to function, cellular energy production comes to a halt, and rapid death follows. HCN being volatile (b.p. 26°C) is more dangerous and can cause death within minutes.
- Cyanide ions are used to extract gold and silver:

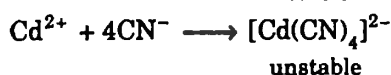
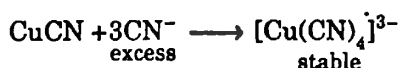
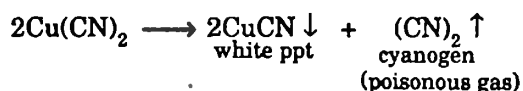
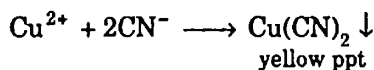


- $\text{Fe}^{2+}(\text{aq})$  combines with  $\text{CN}^-$  forming ferrocyanide (aq) ion,  $[\text{Fe}(\text{CN})_6]^{4-}$ .



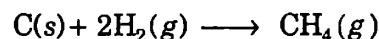
## DEEP Focus

- Mixture of  $\text{Cu}^{2+}(\text{aq})$  and  $\text{Cd}^{2+}(\text{aq})$  can be separated by using  $\text{CN}^-(\text{aq})$ .  $\text{Cu}^{2+}$  form stable  $[\text{Cu}(\text{CN})_4]^{3-}$  and unstable  $[\text{Cd}(\text{CN})_4]^{2-}$  complexes. On passing  $\text{H}_2\text{S}$  gas yellow ppt of  $\text{CdS}$  are obtained without affecting  $[\text{Cu}(\text{CN})_4]^{3-}$  complex.

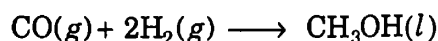


## Illustration 1 Explain coal-gasification.

**Solution** One of the most promising methods for making coal a more efficient and cleaner fuel involves the conversion of coal to a gaseous form, called syngas for “synthesis gas”. This process is called coal gasification. In the presence of very hot steam and air, coal decomposes and reacts according to the following simplified scheme



The main component of syngas is methane. Under suitable conditions, CO and  $\text{H}_2$  combine to form methanol



Syngas is easier than coal to store and transport. It is not a major source of air pollution because sulphur is removed in the gasification process.

## The Carbon Cycle and Green-House Effect

- Carbon cycle is shown by the following scheme (Fig. 12.4)

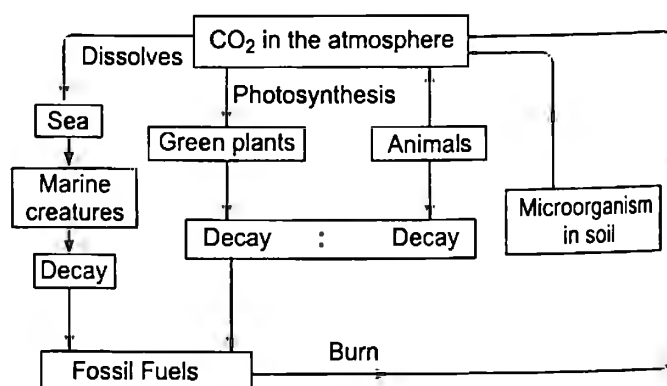


Fig. 12.4 Carbon cycle

Energy from the sun reaches the earth in the form of light. Neither  $\text{CO}_2$  nor  $\text{H}_2\text{O}$  vapour absorbs the visible light so they do not prevent it from reaching the surface of the earth.

- The  $\text{CO}_2$  as well as  $\text{H}_2\text{O}$  absorbs strongly in the infrared region, and its presence in the atmosphere decreases the loss of heat from the earth by radiation. This global warming is called the ‘green house effect’ (other gases, including the oxides of nitrogen from car exhausts, freons from aerosols and refrigerators and methane from bacteria in the soil and in the rumen of cows, also add to the green house effect). The concentration of atmospheric  $\text{CO}_2$  has increased by 10%. This is resulting in the increase in the mean temperature of the earth by 2.5°C, varying from 2°C at the equator to 4°C at the poles (Global

**Warming).** This could have dramatic effects on the climate. The increased temperature would cause more evaporation of water and hence more rain, flooding and tropical storms in certain parts of the world.  $\text{CO}_2$  may dissolve in water and pH of the soil is affected.

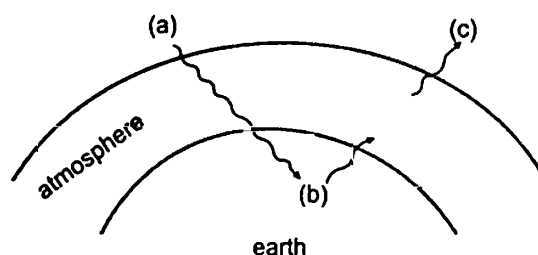
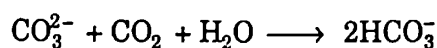
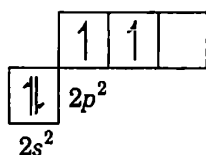


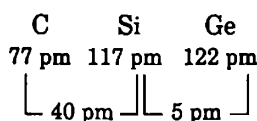
Fig. 12.5 The 'Green-House Effect' (a) Sunlight received by earth, (b) Infrared radiation reradiated by the surface of earth, (c) Infrared radiation emitted to space, following absorption of some of this

## Target Practice 1

1. Tetra covalent nature of the element with following valence shell electronic configuration is explained on the basis of .....



2. Covalent radii of



Show that there is difference of 40 pm while going from C to Si but there is difference of only 5 pm while going from Si to Ge. This is due to

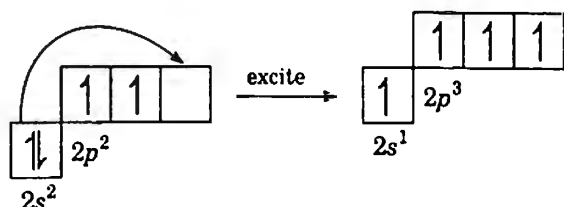
3. (a) Write the element with maximum catenation property. ....
- (b) Write the formulae of compounds/ions in which carbon forms ..... with nitrogen.
- (i) single bond .....
- (ii) double bond .....
- (iii) triple bond .....
4. You have seen electrician joining two points in a circuit by using a wire which is low melting and immediately solidifies.
- (i) What is its name? .....
- (ii) What is the composition? .....
5. Write name/formulae and use of the following

|                     | Name/Formula | Use   |
|---------------------|--------------|-------|
| (i) Dry ice         | .....        | ..... |
| (ii) Semi conductor | .....        | ..... |
| (iii) Solder        | .....        | ..... |
| (iv) TEL            | .....        | ..... |
| (v) CNG             | .....        | ..... |
| (vi) LPG            | .....        | ..... |

6. In the laboratory where you perform chemistry practical, you would have noticed  $\text{NaOH}$  and  $\text{Ca(OH)}_2$  containing reagent bottles with a white coating inside. This coating is of ..... and formed by reaction .....
7. Ni is metal but dissolved in CO gas due to formation of A. A decomposes into metal
- (a) A is .....
- (b) A is formed at a temperature .....
- (c) A decomposes into metal at a temperature .....
8. What are the components in water based fire-extinguisher (a).....(b)..... and reaction releasing  $\text{CO}_2$  is .....
9. Mention two biological/medical uses of  $\text{CO}_2$
- (a) .....
- (b) .....
10. Carbide of magnesium yields propyne on reaction with  $\text{H}_2\text{O}$ . Write bonding structure of this carbide ion. ....
11. Silver containing ore can be converted into silver in cyanide process, with following steps. Write the species formed in
- $\text{Ag} + \text{CN}^- \longrightarrow$  ..... (a)
- $(a) + \text{Zn} \longrightarrow \text{Ag}^+$  ..... (b)
12. In the complex  $[\text{Fe(CN)}_6]^{3-}$  and  $[\text{Fe(CN)}_6]^{4-}$
- (a) Write number of ..... unpaired electrons
- (b) What is magnetic ..... moment
13. When KCN (excess) is added to a  $\text{Cu}^{2+}$  final species formed is ..... and on passing  $\text{H}_2\text{S}$  gas into it .....
14. pH of neutral water is considered as 7. When green house gases dissolve in water, pH will .....
15. There is strong warning due to global warming "New York City will submerge". Comment in three or four lines
- .....
- .....
- .....
- .....

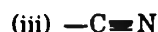
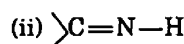
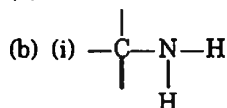
## Answers

1. Excitation of 2s-electrons to 2p-orbital.



2. Refer text

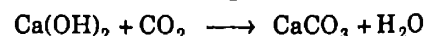
3. (a) Carbon



4. (i) Solder (ii) Sn and Pb

| 5.                  | Name/ Formula           | Use                                           |
|---------------------|-------------------------|-----------------------------------------------|
| (i) Dry ice         | $\text{CO}_2$           | Refrigerant for preserving food               |
| (ii) Semi conductor | Ge                      | Electronic diode triode in computer           |
| (iii) Solder        | Sn/Pb                   | joining circuits                              |
| (iv) TEL            | Tetra ethyl lead        | Anti-knocking compound for petroleum products |
| (v) CNG             | Compressed natural gas  | Eco-friendly fuel for automobiles             |
| (vi) LPG            | Liquefied petroleum gas | Cooking gas                                   |

- 6.
- $\text{Na}_2\text{CO}_3, \text{CaCO}_3$

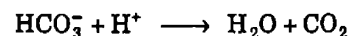


There is also reaction between silicates (of glass) and alkali.

7. (a)
- $\text{Ni(CO)}_4$
- (b)
- $28^\circ\text{C}$
- (c)
- $230^\circ\text{C}$

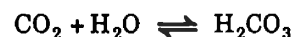
8. (a) Acid (like
- $\text{CH}_3\text{COOH}$
- )

- (b)
- $\text{NaHCO}_3$



9. (a) Photosynthesis

- (b)
- $\text{CO}_2$
- (as
- $\text{HCO}_3^-$
- ) is an important component of buffer of blood which controls pH.



- 10.
- $^-\text{C}\equiv\text{C}-\text{C}^{3-}$

- 11.
- $\text{Ag}^+ + 2\text{CN}^- \longrightarrow [\text{Ag(CN)}_2]^-$
- 
- $2[\text{Ag(CN)}_2]^- + \text{Zn} \longrightarrow \text{Ag} + [\text{Zn(CN)}_4]^{2-}$
- (b)

- 12.
- $[\text{Fe(CN)}_6]^{2-}$
- $[\text{Fe(CN)}_6]^{4-}$
- 
- (a) 1 0

- (b)
- $\sqrt{3}\text{BM}$
- 0

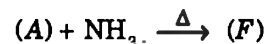
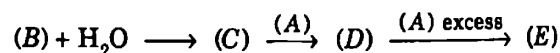
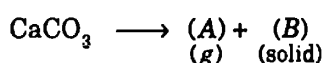
- 13.
- $[\text{Cu(CN)}_4]^{3-}$
- 
- no precipitation takes place being a stable complex.

14. Decrease.

15. Due to global warming, glaciers are melting and due to this sea-level will be certainly increasing which may cause flooding of cities situated at the bank of sea. New York is one of them.

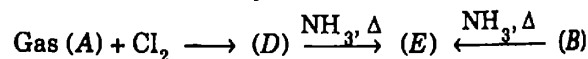
## Practice Exercise 1

- (a) Which theory other than valence bond theory could be used to explain the bonding in  $\text{SiF}_6^{2-}$ ?  
 (b) Predict the shape of this ion.
- Use  $E^\circ$  values given in Table 12.2 to decide whether following reactions are feasible or not?  
 (a)  $\text{Pb}^{4+} + \text{Sn}^{2+} \longrightarrow \text{Sn}^{4+} + \text{Pb}^{2+}$   
 (b)  $\text{Sn}^{4+} + \text{Pb}^{2+} \longrightarrow \text{Pb}^{4+} + \text{Sn}^{2+}$
- Explain :  
 (a)  $(\text{CH}_3)_3\text{N}$  is pyramidal in shape while  $(\text{SiH}_3)_3\text{N}$  is planar.  
 (b) Graphite is a good conductor and diamond is non-conductor.
- Sn and Pb are amphoteric. Explain.
- Sn reacts with  $\text{HNO}_3$  under different conditions. What are various products?
- Sn and Pb dissolve in hot NaOH solution. Write chemical reactions.
- Every year some people die by being in a room containing a faulty heater that uses coal, gas or oil. How might the death occur?
- Identify (A) to (F) in the following:



- 9.
- $\text{H}_2\text{C}_2\text{O}_4 \xrightarrow{\Delta} \text{gas (A)} + \text{gas (B)} + \text{liquid (C)}$
- 
- oxalic acid

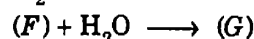
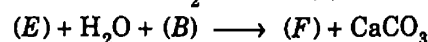
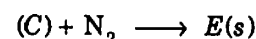
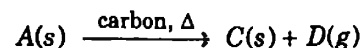
Gas (A) burns with blue flame and is oxidised to gas (B). Gas (B) turns lime water milky.



Identify (A) to (E) and explain reactions.

10. A binary salt (A) on reaction with
- $\text{H}_2\text{O}$
- gives
- $\text{B(aq)}$
- and
- $\text{C(g)}$
- .
- 
- (C) gas on passing into ammoniacal
- $\text{AgNO}_3$
- gives white ppt
- $\text{D(aq)}$
- .
- $\text{CO}_2$
- gas turns
- $\text{B(aq)}$
- milky. Identify (A), (B), (C) and (D).

- 11.
- $\text{CaCO}_3(s) \xrightarrow{\Delta} \text{A(s)} + \text{B(g)}$



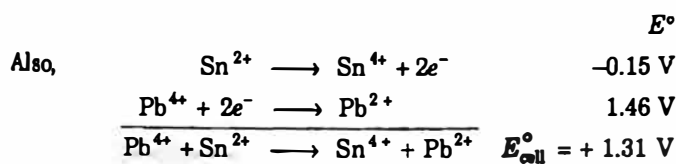
Identify (A) to (G).

12. Give the number of  $\sigma$  and  $\pi$  bonds in (i)  $C_2^{2-}$  (ii)  $C_3^{4-}$  and (iii)  $CN_2^{2-}$ .
13. (i)  $BaC_2 + N_2 \xrightarrow{\Delta} (A)$   
(ii)  $CaC_2 + N_2 \xrightarrow{\Delta} (B)$   
Identify (A) and (B).
14. Is  $CO_2$  the only atmospheric gas responsible for the greenhouse effect.

15. 10 L of a mixture of  $CO$  and  $CO_2$  gas is passed over heated coke when volume increases by 2L. What is % composition of the mixture?
16.  $CO_2$  goes to the atmosphere (greenhouse effect) and thus gets dissolved in  $H_2O$ . pH of the water increases or decreases and what is the effect on the fertility of the soil?
17. Which of the following gases qualify as a greenhouse gas :  $CO$ ,  $NO$ ,  $NO_2$ ,  $Cl_2$ ,  $H_2$ ,  $Ne$ ?

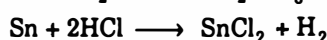
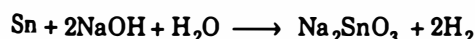
## Answers

1. (a) Molecular orbital theory (b) Octahedral
2. Only (a) feasible due to the fact that stability of  $Pb^{2+} > Pb^{4+}$  and  $Sn^{4+} > Sn^{2+}$



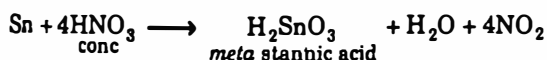
Thus, spontaneous.

3. See text.
4. Both metals react with  $NaOH$  (base) as well as with  $HCl$  (acid), hence are amphoteric :



Similarly with lead.

5.  $4Sn + 10HNO_3 \xrightarrow{\text{dilute}} 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$



6.  $Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2$   
Or  $Sn + 2NaOH + 4H_2O \longrightarrow Na_2[Sn(OH)_6] + 2H_2$

Similarly with Pb.

7. If the flue (chimney) to the heater becomes blocked, or there is insufficient ventilation, the fumes of  $CO$  and  $CO_2$  build up in the room. Unless the person lies on the floor, it is the  $CO$  that kills.

8. (A) :  $CO_2$  (B) :  $CaO$  (C) :  $Ca(OH)_2$  (D) :  $CaCO_3$   
(E) :  $Ca(HCO_3)_2$  (F) :  $NH_2CONH_2$

9. (A) :  $CO$  (B) :  $CO_2$  (C) :  $H_2O$  (D) :  $COCl_2$  (E) :  $NH_2CONH_2$

10. (A) :  $CaC_2$  ( $Ca^{2+}$ ,  $C_2^{2-}$  binary) (B) :  $Ca(OH)_2$  (C) :  $C_2H_2$   
(D) :  $C_2Ag_2$

11. A :  $CaO$  B :  $CO_2$  C :  $CaC_2$  D :  $CO$

E :  $CaCN_2$  (calcium cyanamide nitrolim)

F :  $NH_2CN$  (cyanamide)

G :  $NH_2CONH_2$  (urea)

12. (i)  $C \equiv C^-$  one  $\sigma$ , two  $\pi$  (ii)  $C \equiv C - C^{3-}$  two  $\sigma$ , two  $\pi$   
(iii)  $N \equiv C \equiv N^-$  two  $\sigma$ , two  $\pi$

13. A :  $Ca$  ( $N \equiv C \equiv N$ ) Calcium cyanamide  
Ba ( $C \equiv N$ )<sub>2</sub> barium cyanide.

14. There are several gases that are even stronger infrared absorbers than  $CO_2$  [for example  $CH_4$ ,  $O_3$ ,  $N_2O$ , chlorofluoro carbons (CFC)]. About one-half of the anticipated greenhouse effect is due to  $CO_2$  and the remainder of these other gases. Furthermore, the atmospheric concentration of some of these other gases (especially CFC) have been growing at a faster rate than  $CO_2$ .

15.  $CO_2 + C \xrightarrow{\Delta} 2CO$

$$\begin{array}{l} \text{let} \quad CO_2 = x \text{ L} \\ \quad \quad CO = (10 - x) \text{ L} \end{array}$$

$CO$  due to passage over heated coke =  $2x$  (from  $CO_2$ , no effect on  $CO$ , already in mixture)

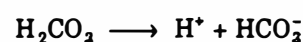
$$\text{Thus,} \quad 10x + 2x = 12$$

$$x = 2L$$

$$\text{Thus,} \quad CO_2 = 2L, 20\%$$

$$CO = 8L, 80\%$$

16.  $CO_2 + H_2O \rightleftharpoons H_2CO_3$



$[H^+]$  increases hence pH decreases. Fertility of the soil also decreases.

17.  $CO$ ,  $NO$  and  $NO_2$

## Silicon

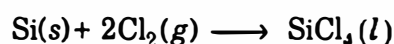
### Isolation of Silicon

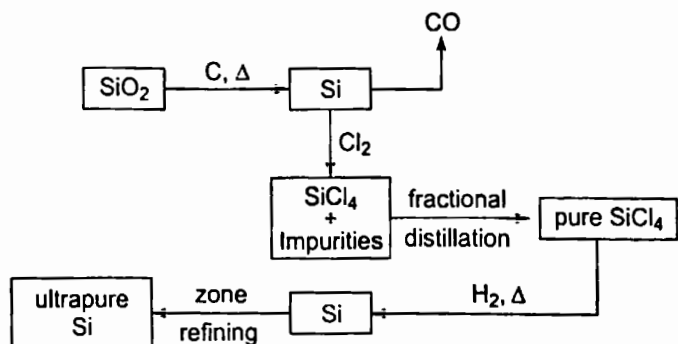
Silicon is a hard grey, semiconducting solid that melts at  $1410^\circ C$ . It crystallises in a diamond like structure but does not form a graphite allotrope because of the relatively poor overlap of silicon  $\pi$  orbitals. In nature, silicon is generally found combined with oxygen in  $SiO_2$  and in various silicate minerals.

It is obtained in elemental form by reduction of silica sand ( $SiO_2$ ) with coke (C) in an electric furnace :



The silicon used for making solid-state semiconductor devices such as transistors, computer chips, and solar cells must be ultrapure, with impurities at a level of less than  $10^{-7}\%$  (1 ppb). Silicon is purified by converting it to  $SiCl_4$ , a volatile liquid (b.p.  $58^\circ C$ ) that can be separated from impurities by fractional distillation and then converted back to elemental silicon by reduction with hydrogen.





The silicon is purified further by a process called **zone refining** (Fig. 12.6). In this process, a heater melts a narrow zone of a silicon rod. Impurities concentrate in the molten zone and as the heater sweeps slowly down the rod, ultrapure silicon crystallises at the trailing zone of the molten zone.

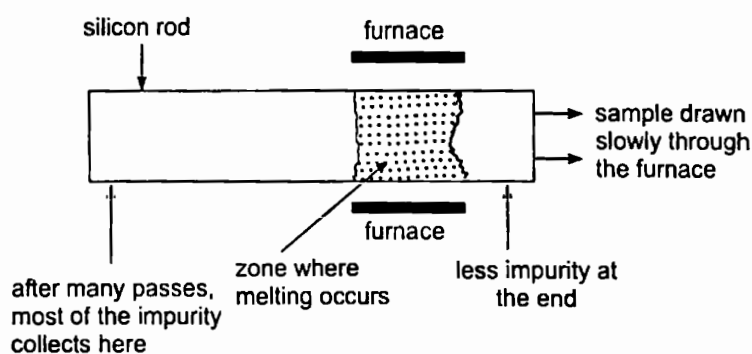


Fig. 12.6 Zone-refining. The sample is passed through the furnace many times. The impurities collect at one end of the

## Compounds of Silicon

- A silicon atom, like a carbon atom, can form four bonds simultaneously. It uses all of its valence electrons ( $3s^2 3p^2$ ) in an  $sp^3$  hybridisation scheme, and crystallises in an fcc structure similar to diamond. There is no allotrope of silicon equivalent to the graphite. **Diamond is an electrical insulator,**

**graphite is good electrical conductor but silicon is a semiconductor.**

|          |               |
|----------|---------------|
| Diamond  | Insulator     |
| Graphite | Conductor     |
| Silicon  | Semiconductor |

- Silicon is one of the most abundant of elements, being the essential ingredient of a large number of minerals that make up the earth's surface.

## Silicates

- The majority of the compounds consist of silicates, in which silicon and oxygen make **giant** three dimensional structures. They are all based on the same base building block made from one silicon atom and four oxygen atoms at the corners of a tetrahedron. These  $\text{SiO}_4$  tetrahedra may be :
  - separate units,
  - joined into chains or rings in groups of 2, 3, 4 or 6,
  - joined together into long single or double chains,
  - arranged in sheets,
  - linked into three dimensional network.
- The name '**silica**' covers an entire group of minerals, which have the general formula  $\text{SiO}_2$ , the most common of which is **quartz**. Quartz is a framework silicate with  $\text{SiO}_4$  tetrahedra arranged in spirals. *The spirals can turn in a clockwise or anti-clockwise direction—a feature that results in there being two mirror image, optically active, varieties of quartz.* Quartz is used as a piezoelectric material (crystal oscillators and transducers). Silica gel and fumed silica are amorphous forms of silica. Silica gel is formed when sodium silicate is acidified, and its dehydrated form is a drying agent in chromatography and catalyst support. Some silicate minerals are summarised in Table 12.5.

Table 12.5 Some Representative Silicate Minerals

| Type                               | Anion type                       | Mineral        | Composition                                                                                                                                 |
|------------------------------------|----------------------------------|----------------|---------------------------------------------------------------------------------------------------------------------------------------------|
| 1. Ortho silicate (neso-silicates) | $\text{SiO}_4^{4-}$              | zircon olivine | $\text{ZrSiO}_4, \text{Mg}_2\text{SiO}_4$                                                                                                   |
| 2. Pyrosilicate (soro-silicates)   | $\text{Si}_2\text{O}_7^{6-}$     | thortveitite   | $\text{Sc}_2\text{Si}_2\text{O}_7$                                                                                                          |
|                                    | $\text{Si}_6\text{O}_{18}^{12-}$ | beryl          | $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$                                                                                            |
| 3. Pyroxene                        | Si—O chains                      | spodumene      | $\text{LiAl}(\text{SiO}_3)_2$                                                                                                               |
| 4. Amphibole                       | Si—O double chains               | hornblende     | $(\text{Ca}, \text{Na}, \text{K})_{2-3} (\text{Mg}, \text{Fe}, \text{Al})_5 (\text{Si}, \text{Al})_2 \text{Si}_6\text{O}_{22}(\text{OH})_2$ |
| 5. Mica                            | Si—O sheets                      | muscovite      | $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$                                                                                     |
| 6. Zeolite                         | Si—O three-D network             | natrolite      | $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{12} \cdot 2\text{H}_2\text{O}$                                                                  |
| 7. Single-chain silicate           | $\text{SiO}_4^{4-}$              | diopside       | $[\text{CaMg}(\text{SiO}_3)_2]_n$                                                                                                           |
| 8. Double-chain silicate           | $\text{SiO}_4^{4-}$              | asbestos       | $[\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2]_n$                                                                       |
| 9. Sheet-like silicate             | $\text{SiO}_4^{2-}$              | talc           | $[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2]_n$                                                                                      |

- The vast majority of silicates are insoluble in water; only the simple alkali metal silicates are soluble.
- The extreme stability of the silicates is due to the donation of extra electrons from O atoms into vacant 3d orbitals of Si.
- In many common minerals, called **aluminosilicates**, Al atoms replace some Si atoms with very little structural change. In such cases univalent cations such as  $K^+$  or  $Na^+$  are also joined to balance positive charge of Si.

### DEEP Focus

Following points are helpful in understanding the structural principles in silicates :

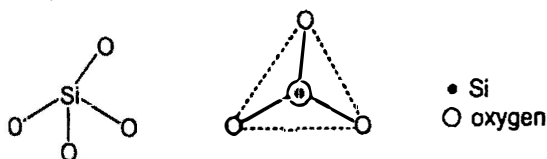
(a) The strong Si—O bond ( $\Delta H = 466 \text{ kJ mol}^{-1}$ ) may be considered 50% ionic and 50% covalent from electronegativity difference (which is  $3.5 - 1.8 = 1.7$ ).

(b) The radii of  $Si^{4+}$  ion and  $O^{2-}$  ion are 0.40 and 1.40 Å respectively. The radius ratio 0.29 concludes coordination number 4 around Si which is in agreement with  $sp^3$  hybridized tetrahedral arrangement around Si.

(c) The radius of  $Al^{3+}$  ion (0.53 Å) is close to that of the  $Si^{4+}$  ion and thus  $Al^{3+}$  can replace  $Si^{4+}$  in many silicates. Monovalent cation as  $Na^+$  or  $K^+$  maintains electrical neutrality. A pair of ions like ( $Si^{4+} + Na^+$ , total charge +5) may also be replaced by isoelectrical ion pairs like ( $Al^{3+} + Mg^{2+}$ ) or ( $Al^{3+} + Ca^{2+}$ ).

(d) The  $SiO_4$  tetrahedral units may occur singly or may share one, two, three or four O-atoms through corners giving rise to cyclic groups, chains, infinite layers or infinite three-dimensional frameworks.

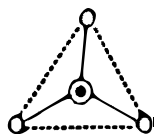
(e)  $SiO_4^{4-}$  unit is represented as



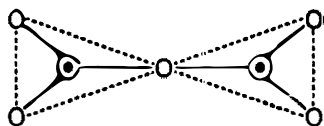
Taking above facts we consider following cases (also refer Table 12.5).

**Case I:** No oxygen atom shared (orthosilicate)

Unit :  $SiO_4^{4-}$



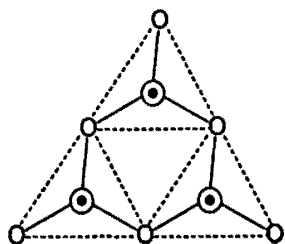
**Case II:** One oxygen atom shared (pyrosilicate)



Unit :  $Si_2O_7^{6-}$  ion, two  $SiO_4$  units joined by sharing an oxygen atom.

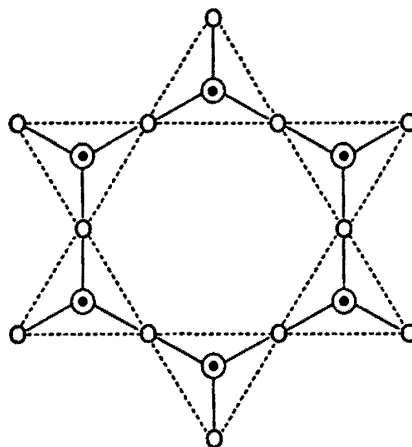
**Case III:** Two oxygen atoms shared (closed ring : cyclosilicates and continuous chains : inosilicates)

Each  $SiO_4$  tetrahedron shares an O-atom with each of two neighbouring tetrahedra resulting ring or chain anions



**Ring anions :** (1)  $Si_3O_9^{6-}$ —three  $SiO_4$  tetrahedra linked together as in benitoite ( $BaTiSi_3O_9$ ) and in wollastonite ( $Ca_3Si_3O_9$ ).

(2)  $Si_6O_{18}^{12-}$ —six  $SiO_4$  tetrahedra linked together as in beryl ( $Be_3Al_2Si_6O_{18}$ )



### Chain-Silicate Anions

The minerals having silicate chains are collectively called pyroxenes :  $MgSiO_3$ ,  $CaMg(SiO_3)_2$ .

Double chains result by joining two simple chains by sharing oxygens. Examples are :

**Amphiboles** having anions like  $Si_4O_{11}^{6-}$

Asbestos mineral as **tremolite**  $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$

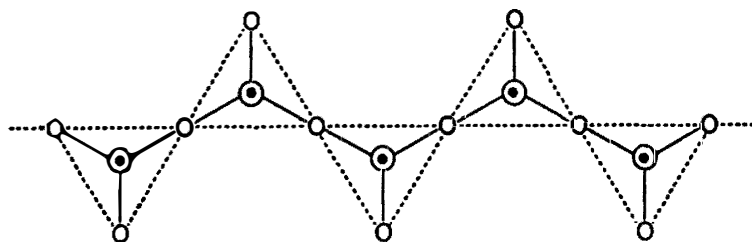
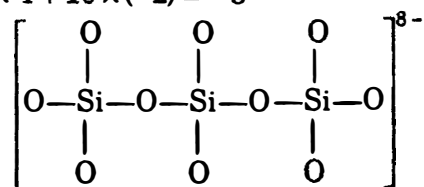


**Illustration 1** The silicate anion in the mineral *kinoite* is a chain of three  $SiO_4$  tetrahedra that share corners with adjacent tetrahedra. The mineral also contains  $Ca^{2+}$  ions,  $Cu^{2+}$  ions, and water molecules in a 1:1:1 ratio.

(a) Give the formula and charge of the silicate anion

(b) Give the complete formula for the mineral

**Solution** (a) The silicate anion has three  $SiO_4$  tetrahedra that share corners with adjacent tetrahedra thus silicate is  $Si_3O_{10}$ , hence it can be represented as with charge as  $= 3 \times 4 + 10 \times (-2) = -8$



(b)  $Ca^{2+}$ ,  $Cu^{2+}$  and  $H_2O$  are in the ratio of 1:1:1 and to balance  $(-8)$  charge of silicate anion,  $(+8)$  charge is required thus there are two units each of  $Ca^{2+}$ ,  $Cu^{2+}$  and  $H_2O$  thus, kinoite has formula  $Ca_2Cu_2Si_3O_{10} \cdot 2H_2O$ .

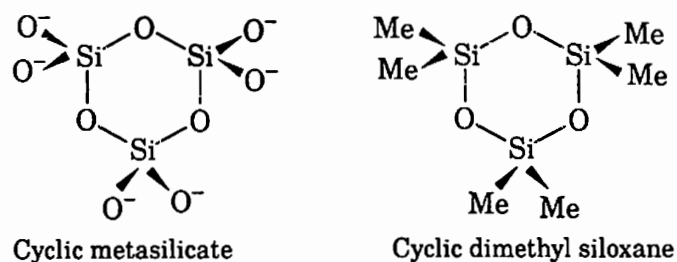
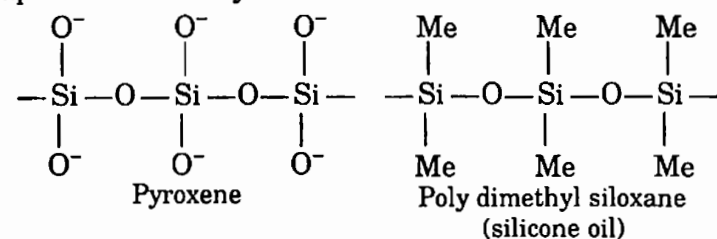


## Silicones

Silicones are synthetic organo-silicon polymers containing repeated  $R_2SiO$  units. Since the empirical formula is that of a ketone ( $R_2CO$ ), the name silicone has been given to these materials. Silicones can be made into oils, rubbery elastomers and resins. They find a variety of applications because of their

- (i) chemical inertness
- (ii) water-repelling nature
- (iii) heat-resistance
- (iv) good electrical insulating property
- (v) high thermal stability
- (vi) resistant to UV rays
- (vii) anti-foam characteristics
- (viii) non-toxicity
- (ix) non-stick property
- (x) physiological inertness

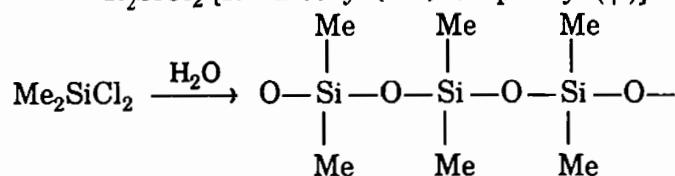
The wide range of chain, cyclic and cross-linked silicone polymers are based on structural patterns similar to those in silicates. For example, the  $O^-$  in silicates have been replaced by the formally isoelectronic  $CH_3(Me)$  groups in the dimethyl silicones



Both silicones and silicates are formed due to the reluctance of silicon to form silicon to oxygen double bonds. But the silicates are all solids while the silicones may be oils; greases, rubbers or resins depending upon the extent of polymerisation.

Commercial silicon polymers are usually methyl derivatives and to a lesser extent phenyl derivatives and are synthesised by the hydrolysis of chlorosilanes.

$R_2SiCl_2$  [ $R$  = methyl (Me) or phenyl ( $\phi$ )]



Thus, synthesis of silicones involves two steps

**Step I** Preparation of chlorosilanes

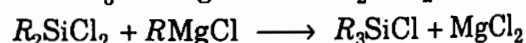
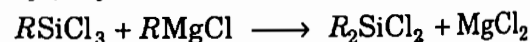
**Step II** Hydrolysis of chlorosilanes to silanols and then to silicones

**Step I** Chlorosilanes may be prepared by the

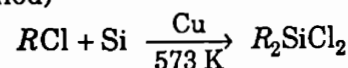
(i) reaction of Grignard reagent with  $SiCl_4$



( $R$  = alkyl, aryl)



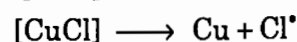
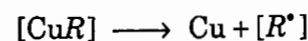
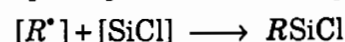
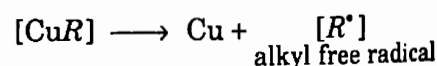
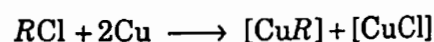
(ii) reactions of alkyl halides with silicon (Rochow direct method)



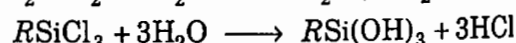
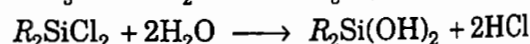
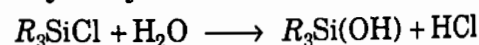
Nature of chlorosilanes may be changed by changing molar concentration of  $RCl$ .

Above reaction is exothermic hence in the course of the reaction, removal of heat is necessary to make better yield.

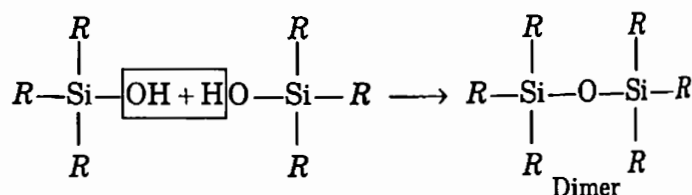
Free radicals are involved as the intermediates.



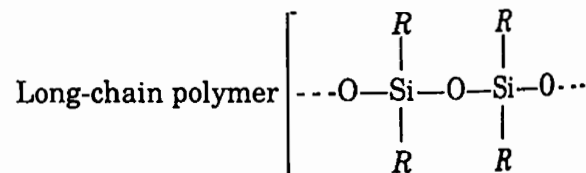
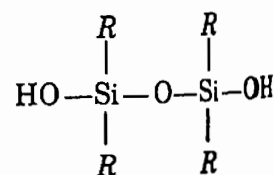
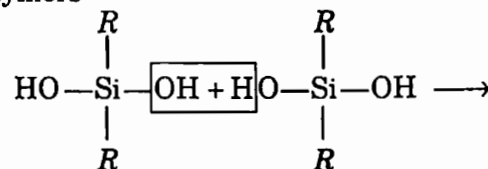
**Step II** Hydrolysis of chlorosilanes to silanol



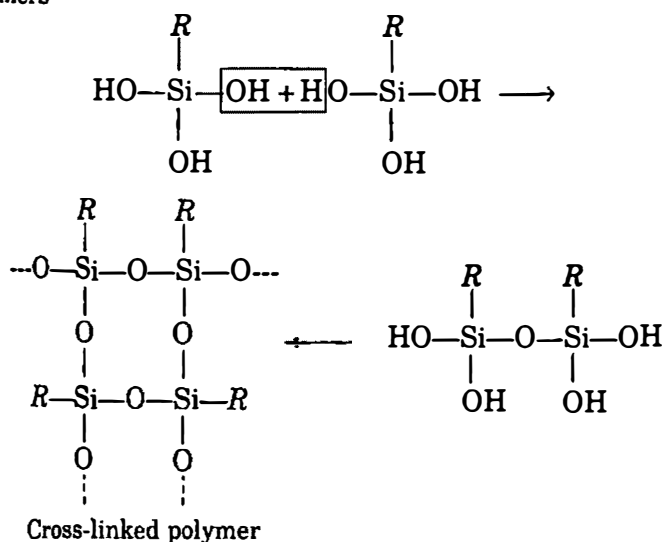
**Case I** Silanol,  $R_3Si(OH)$  undergoes dimerisation



**Case II** Disilanol,  $R_2Si(OH)_2$  produces long-chain polymers



**Case ■** Trisilanol,  $\text{RSi(OH)}_3$  produces cross-linked polymers



As the degree of polymerisation increases, silicones may be changed to solid state from liquid state.

- Liquid (oils)
- Semi-solids (greases)
- Elastomers (rubbers)
- Solids (resins)

Some special adhesives are made by mixing two silicones-based materials, which react together when mixed to give a cross-linked polymer.

The hydrolysis is usually initiated by a small quantity of concentrated  $\text{H}_2\text{SO}_4$  but  $\text{KOH}$  may also be used to prepare certain silicone rubbers. Hydrolysis of  $\text{PhSiCl}_3$  ( $\text{Ph}$  = phenyl) and  $\text{PhSiCl}_2$  in toluene produces silicone resins. The polymerisation is allowed to proceed to a stage when the products is still soluble in toluene. It is shaped or moulded in this form and heated to  $200^\circ\text{C}$  in presence of a catalyst (a quaternary ammonium compound) when cross-linking develops the final 3-D network, by condensing the remaining  $\text{OH}$  groups.

Given properties of the silicones may be related to their silica like ( $\text{Si}-\text{O}-\text{Si}-\text{O}$ ) skeleton surrounded by alkyl groups which make them water-repelling.

Silicone fluids containing straight chain polymers (20-50 units) are used in making cement work and fibres water-repellant, as dielectric insulating media (in high voltage transformer), hydraulic oils and light duty lubricating oil. Mixed with lithium stearate soaps, they make quality grease for use in high vacuum apparatus. Silicone oils are also useful broad spectrum anti-foaming agents.

Silicone rubbers are made by reinforcing straight chain polymers (having  $6 \times 10^3$  to  $6 \times 10^5$  Si units) with fillers like  $\text{SiO}_2$  or graphite. They can be 'vulcanised' by increasing cross links through oxidations with benzoyl

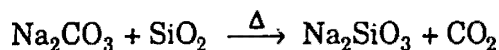
peroxide. These rubbers retain their quality from  $-100^\circ\text{C}$  to  $250^\circ\text{C}$ . Such rubbers find extensive uses as industrial sealants and adhesives, space suits, medical tubing, etc.

Silicone resins are used in electrical insulations, as laminates for printed circuit boards or in encapsulation resistors, integrated circuit, etc. They are used in coating cooking ware and industrial tyre moulds.

## Glass

Solids are most stable in crystalline form. However, if a solid is formed rapidly (for example, when a liquid is cooled quickly), its atoms or molecules do not have time to align themselves and may become locked in positions other than those of a regular crystal.

If we mix sodium carbonate and calcium carbonate with sand and fuse the mixture at about  $1500^\circ\text{C}$ , we get a liquid mixture of sodium and calcium silicates. When this mixture is cooled, it becomes viscous and eventually ceases to flow; it becomes solid—called glass. **Glass is thus super-cooled liquid (solid solution).** Amorphous solids, such as glass, lack regular three dimensional arrangement of atoms. **Glass thus refers to an optically transparent fusion product of inorganic materials that has cooled to a rigid state without crystallising.**



By varying the proportions of the three basic ingredients, and by adding other substances, we can alter the properties of the glass as given :

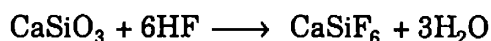
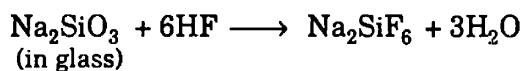
- Calcium-alkali silicate glass — normal domestic glass for windows
- |                                                                   |                                                                                              |
|-------------------------------------------------------------------|----------------------------------------------------------------------------------------------|
| Sodium silicate                                                   | — soda glass used in cheap laboratory glassware                                              |
| Potassium silicate                                                | — potash glass                                                                               |
| PbO (if CaO in glass is replaced by PbO)                          | — lead glass has a higher refractive index used in making optical parts and glass ornaments. |
| $\text{B}^{3+}$ replaces some $\text{Si}^{4+}$ in the tetrahedral | — borosilicate glass—used in heat resistant glasswares (Pyrex)                               |
- Fining agents such as  $\text{NaNO}_3$  or  $\text{As}_2\text{O}_3$  are added to remove bubbles.
- Decolourising agents may be added to eliminate impurities and to obtain colourless glass.  $\text{CaF}_2$  is sometimes added to make opal glass.
- The colour of glass is due largely to the presence of metal ions (as oxides)

| Colour of glass | Metal oxide                          |
|-----------------|--------------------------------------|
| Green           | Fe <sub>2</sub> O <sub>3</sub> , CuO |
| Yellow          | UO <sub>2</sub>                      |
| Blue            | CuO, CoO                             |
| Red             | Colloidal Cu, Au                     |

Following table shows the composition and properties of quartz, Pyrex, and soda-lime glass.

| Name              | Composition                                                                                                    | Properties and uses                                                                                                                               |
|-------------------|----------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|
| Pure quartz glass | 100% SiO <sub>2</sub>                                                                                          | Low thermal expansion, transparent to wide range of wavelengths; used in optical research.                                                        |
| Pyrex glass       | SiO <sub>2</sub> : 60–80%<br>B <sub>2</sub> O <sub>3</sub> : 10–25%<br>Al <sub>2</sub> O <sub>3</sub> : small% | Low thermal expansion; transparent to visible and infrared, but not to UV radiation; used mainly in laboratory and household cooking glassware.   |
| Soda-lime glass   | SiO <sub>2</sub> : 75%<br>Na <sub>2</sub> O : 15%<br>CaO : 10%                                                 | Easily attacked by chemicals and sensitive thermal shocks. Transmits visible light, but absorbs UV radiation; used mainly in windows and bottles. |

Glass is attacked by HF and this property is used to make marking on the glass (**etching**)



HF, however does not attack wax. The portion of the glass on which **etching** is to be done is covered with wax layer. Markings are carved on the wax layer with a pin and HF is poured on the carved parts and left for sometime. After washing with water, wax is removed and permanent marking is obtained.

## Ceramics

Ceramics are inorganic, non-metallic, non-molecular solids, including both crystalline materials such as quartz (SiO<sub>2</sub>) and amorphous materials such as glasses. Traditional silicate ceramics, such as pottery and porcelain are made by heating aluminosilicate clays to high temperatures. Modern, so-called **advanced ceramics** materials that have hightech engineering, electronic and biomedical applications include oxide ceramics, such as alumina (Al<sub>2</sub>O<sub>3</sub>), and non-oxide ceramics, such as alumina carbide (SiC) and silicon nitride. Additional examples are given in Table 12.6 which compares properties of ceramics with those of aluminium and steel.

Table 12.6 Properties of Some Ceramic and Metallic Materials

| Material                                        | M.P/°C | Density/g cm <sup>-3</sup> |
|-------------------------------------------------|--------|----------------------------|
| Oxide ceramics                                  |        |                            |
| Alumina, Al <sub>2</sub> O <sub>3</sub>         | 2072   | 4.0                        |
| Beryllia, BeO                                   | 2530   | 3.0                        |
| Zirconia, ZrO <sub>2</sub>                      | 2700   | 5.9                        |
| Non-oxide ceramics                              |        |                            |
| Boron carbide, B <sub>4</sub> C                 | 2350   | 2.5                        |
| Silicon carbide, SiC                            | 2700   | 3.2                        |
| Silicon nitride, Si <sub>3</sub> N <sub>4</sub> | 1900   | 3.4                        |
| Metals                                          |        |                            |
| Aluminium                                       | 660    | 2.7                        |
| Plain carbon steel                              | 1515   | 7.9                        |

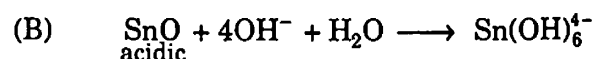
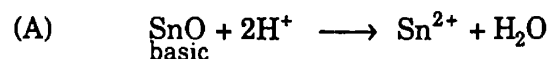
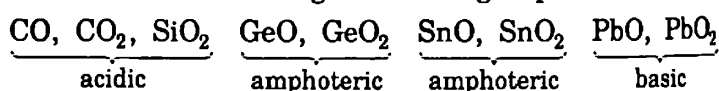
## Compounds of Tin

### Tin oxides

Two types of oxides are known :

SnO and SnO<sub>2</sub>

Both are amphoteric. As we know, basic character of oxides increases as we go down the group.



In (A), SnO reacts with H<sup>+</sup>, hence SnO is basic oxide.

In (B), SnO reacts with OH<sup>-</sup>, hence SnO is an acidic oxide.

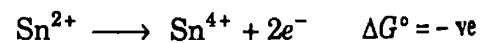
These two reactions confirm that SnO is an amphoteric oxide.

[Sn(OH)<sub>6</sub>]<sup>4-</sup> or [Sn(OH)<sub>3</sub>]<sup>-</sup> is called stannite ion and is also written as HSnO<sub>2</sub><sup>-</sup> and SnO<sub>2</sub><sup>2-</sup>. [Sn(OH)<sub>6</sub>]<sup>2-</sup> is called stannate ion and is also written as SnO<sub>3</sub><sup>2-</sup> and SnO<sub>4</sub><sup>4-</sup>.

### Tin Chlorides

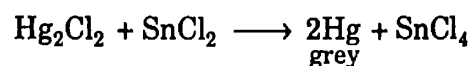
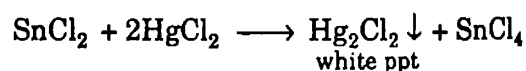
SnCl<sub>2</sub> [tin (II) chloride] is obtained by dissolving tin in concentrated HCl; on cooling crystals of SnCl<sub>2</sub> · 2H<sub>2</sub>O separate out. Anhydrous SnCl<sub>2</sub> is formed by heating Sn in a current of HCl vapour.

SnCl<sub>2</sub> and SnCl<sub>4</sub> are common chlorides but due to 'inert-pair effect', Sn(II) is less stable than Sn(IV), hence the reaction



is spontaneous. Thus Sn<sup>2+</sup> salts are reducing agents.

- SnCl<sub>2</sub> reduces HgCl<sub>2</sub> first to Hg<sub>2</sub>Cl<sub>2</sub> and then to Hg.

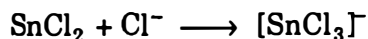


- $\text{SnCl}_2$  reduces  $\text{FeCl}_3$  to  $\text{FeCl}_2$   

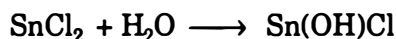
$$2\text{FeCl}_3 + \text{SnCl}_2 \longrightarrow 2\text{FeCl}_2 + \text{SnCl}_4$$
- It also reduces  $\text{CuCl}_2$  to  $\text{CuCl}$   

$$\text{SnCl}_2 + 2\text{CuCl}_2 \longrightarrow \text{SnCl}_4 + 2\text{CuCl} \downarrow$$

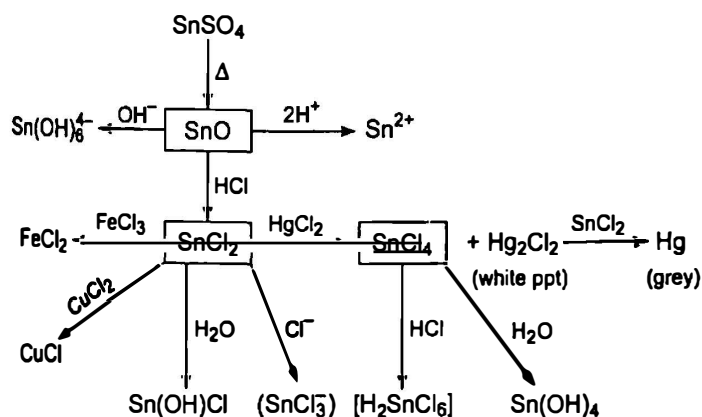
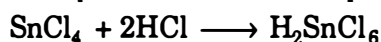
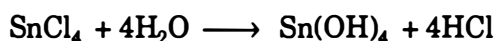
white ppt
- $\text{SnCl}_2$  (and also  $\text{SnF}_2$ ) dissolve in solutions containing  $\text{Cl}^-$  (or  $\text{F}^-$ ) ions



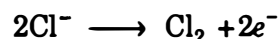
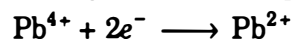
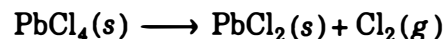
- $\text{SnCl}_2$  partly hydrolyses in water forming the basic chloride  $\text{Sn(OH)Cl}$



- $\text{SnCl}_4$  also hydrolyses in dilute solution but it is incomplete and can be repressed in presence of halogen acid :

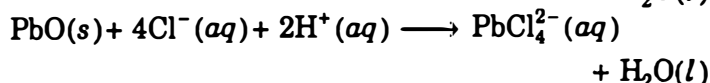
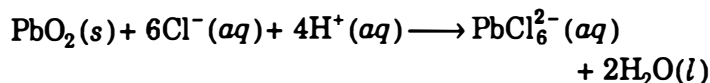


- $\text{PbCl}_4$  decomposes very readily into  $\text{PbCl}_2$  and  $\text{Cl}_2$  due to greater stability of  $\text{Pb}^{2+}$  than  $\text{Pb}^{4+}$  (inert-pair effect)



Thus,  $\text{Pb}^{4+}$  salts are better oxidising agents.

- Lead shows the ability to make a complex with chloride ions. If ice cold conc.  $\text{HCl}$  is added to lead dioxide [lead (IV) oxide],  $\text{PbO}_2$ , yellow hexachloro plumbate (IV) ions,  $[\text{PbCl}_6]^{2-}$  are made.  $[\text{PbCl}_4]^{2-}$  are made from  $\text{PbO}$



## Lead oxides

Three oxides of lead are known :

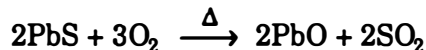
(a)  $\text{PbO}$  — lead (II) oxide called **litharge** (a yellow-

orange solid)

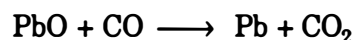
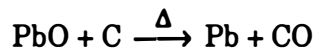
(b)  $\text{PbO}_2$  — lead (IV) oxide also called **lead dioxide** (a dark brown solid)

(c)  $\text{Pb}_3\text{O}_4$  — dilead (II) lead (IV) oxide. It is a combination of (a) and (b) :  $2\text{PbO} \cdot \text{PbO}_2$ . It is also called **red lead**.

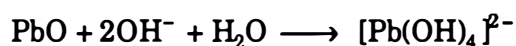
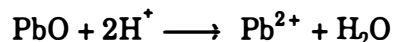
- $\text{PbO}$  is obtained by roasting of  $\text{PbS}$  (galena):



$\text{PbO}$  is reduced to  $\text{Pb}$  by heating with carbon:

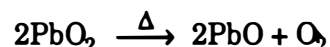
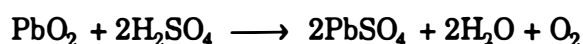
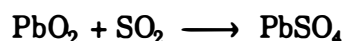
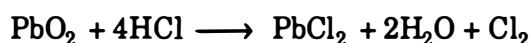
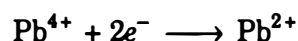


$\text{PbO}$  is amphoteric, being soluble both in acid and alkali:

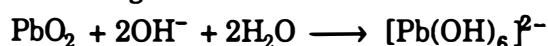


Crystal structure shows that it is predominantly covalent character.

- $\text{PbO}_2$  is an oxidising agent and reduced to  $\text{PbO}$  since stability of  $\text{Pb(II)} > \text{Pb(IV)}$  based on 'inert pair' effect:



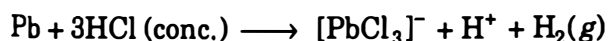
It is insoluble in an acid but soluble in concentrated alkali thus indicating its acidic nature:



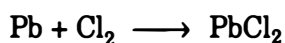
## Compounds of Lead

### Lead Chlorides

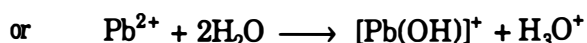
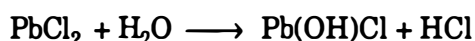
- Lead reacts with dil.  $\text{HCl}$  producing insoluble  $\text{PbCl}_2$  which protects the metal from further attack. But due to the formation of the soluble complex ion  $[\text{PbCl}_3]^-$ ,  $\text{PbCl}_2$  dissolves in conc.  $\text{HCl}$ . Thus lead dissolves in conc.  $\text{HCl}$ .



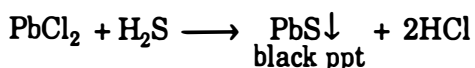
- $\text{Pb}$  can also be converted into  $\text{PbCl}_2$  on reaction with  $\text{Cl}_2$ :



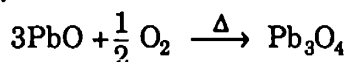
- $\text{PbCl}_2$  is partially hydrolysed by  $\text{H}_2\text{O}$  :



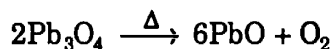
- Aqueous hot solution of  $\text{PbCl}_2$  gives black ppt of  $\text{PbS}$  on passing  $\text{H}_2\text{S}$  gas:



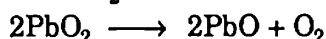
- $\text{Pb}_3\text{O}_4$ , a double oxide, is obtained by heating lead (II) oxide in air:



Its crystal structure shows that it is predominantly covalent and composed of a combination of two types of lead atom. One type is bonded to six oxygen atoms, the other to three oxygen atoms. But in the reactions, it behaves like a mixture of  $\text{PbO}$  and  $\text{PbO}_2$ :

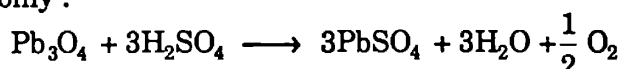


$\text{Pb}_3\text{O}_4$  can be written as:



and out of two oxides only  $\text{PbO}_2$  is affected by heat:

When it reacts with  $\text{H}_2\text{SO}_4$ ,  $\text{PbSO}_4$  is formed along with  $\text{O}_2$  only:

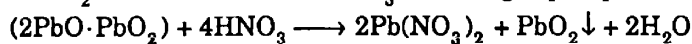


### DEEP Focus

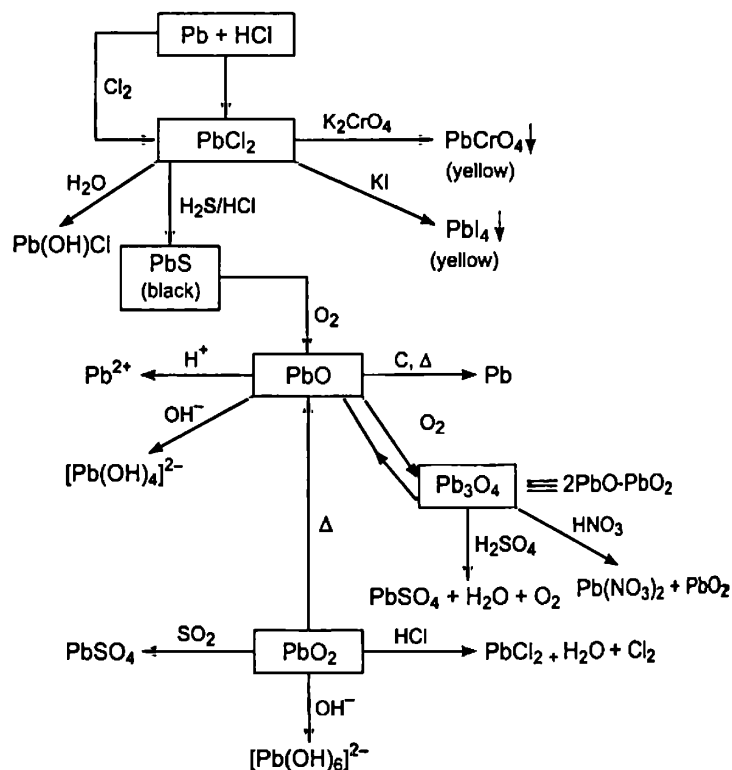
With  $\text{HNO}_3$ ,  $\text{PbO}_2$  is precipitated and soluble  $\text{Pb}(\text{NO}_3)_2$  is also formed:



This reaction clearly indicates that  $\text{Pb}(\text{NO}_3)_2$  is from  $\text{PbO}$  while  $\text{PbO}_2$  remains insoluble in  $\text{HNO}_3$  and thus gets precipitated:

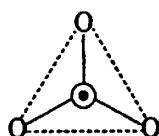


Lead oxides are used in the manufacture of lead-acid (storage) batteries, glass, ceramic glazes, cements ( $\text{PbO}$ ), metal protecting paints ( $\text{Pb}_3\text{O}_4$ ), matches ( $\text{PbO}_2$ ), and explosives ( $\text{PbO}_2$ ).



## Target Practice 2

- $\text{SiO}_4^{4-}$  unit is represented as



• Si  
O oxygen

Represent  $\text{Si}_2\text{O}_7^{6-}$  similarly such that one oxygen atom is shared between two units of  $\text{SiO}_4$ .

- Silicones are .....
  - They are formed when ..... reacts with .....
  - They are used as .....
  - Write structure of simple silicone.

- A lab assistant was employed in a chemical industry manufacturing  $\text{NaOH}$ ,  $\text{HF}$  and  $\text{HNO}_3$ . He was given three vessels for storing these chemicals. Can you help in exact matching without any loss to the vessel.

**Chemicals:**  $\text{NaOH}$ ,  $\text{HF}$ ,  $\text{HNO}_3$ .

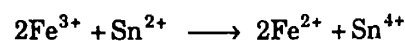
**Vessels made of:** Al, glass, wax

Matching is: (i)  $\text{NaOH}$  .....

(ii)  $\text{HF}$  .....

(iii)  $\text{HNO}_3$  .....

- $\text{SnCl}_2$  can be volumetrically determined by titration with  $\text{FeCl}_3$



Can you write the suitable indicator based on previous sections.

- $\text{SnO}$  is called an amphoteric oxide. You are asked to prove this statement then chemicals required are

(a) ..... (b) .....

- I.  $[\text{Sn(OH)}_6]^{4-}$  can be represented as ..... or .....  
(a) ..... (b) .....

and is called .....

(c)

- II.  $[\text{Sn(OH)}_6]^{2-}$  can be written as ..... or .....  
(a) ..... (b) .....

and is called .....

(c)

- Write the products when  $\text{Pb}_3\text{O}_4$  reacts with

(a)  $\text{HCl} \longrightarrow$  .....

(b)  $\text{H}_2\text{SO}_4 \longrightarrow$  .....

(c)  $\text{HNO}_3 \longrightarrow$  .....

- Following reactions are spontaneous not.

(a)  $\text{PbO}_2 \longrightarrow \text{PbO} + \text{O}_2$

Yes/No

(b)  $\text{PbCl}_4 \longrightarrow \text{PbCl}_2 + \text{Cl}_2$

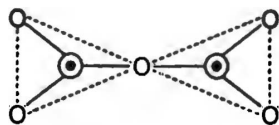
Yes/No

- (c)  $\text{SnCl}_4 + \text{PbCl}_2 \longrightarrow \text{PbCl}_4 + \text{SnCl}_2$  Yes/No  
 (d)  $2\text{FeCl}_3 + \text{SnCl}_2 \longrightarrow \text{SnCl}_4 + 2\text{FeCl}_2$  Yes/No  
 9. An oxide of lead changes to another insoluble oxide and soluble salt on reaction with  $\text{HNO}_3$

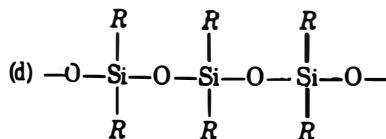
- (a) oxide is .....  
 (b) insoluble oxide is .....  
 (c) soluble salt is .....

### Answers

1.  $\text{Si}_2\text{O}_7^{6-}$  ion with two  $(\text{SiO}_4)$  units joined by sharing as oxygen atom.



2. (a) Synthetic polymers containing repeated  $\text{R}_2\text{SiO}$ .  
 (b)  $\text{R}_2\text{SiCl}_2, \text{H}_2\text{O}$   
 (c) Refer text



3. (i)  $\text{NaOH}$  : Glass  
 (ii)  $\text{HF}$  : Wax  
 (iii)  $\text{HNO}_3$  : Al  
 4.  $\text{KCNS}$ , its gives red colour with  $\text{Fe}^{3+}$  ion.  
 5. (a)  $\text{HCl}$  (b)  $\text{NaOH}$   
 6. I : (a)  $\text{HSnO}_2^-$  (b)  $\text{SnO}_2^{2-}$  (c) stannite ion  
 II : (a)  $\text{SnO}_3^{2-}$  (b)  $\text{SnO}_4^{4-}$  (c) stannate ion  
 7. (a)  $\text{Pb}_3\text{O}_4 + 4\text{HCl} \longrightarrow 2\text{PbCl}_2 + \text{PbO}_2 + 2\text{H}_2\text{O}$   
 $\text{PbO}_2 + 4\text{HCl} \longrightarrow \text{PbCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$   
 (b)  $\text{Pb}_3\text{O}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow 3\text{PbSO}_4 + 3\text{H}_2\text{O} + \frac{3}{2}\text{O}_2$   
 (c)  $\text{Pb}_3\text{O}_4 + 4\text{HNO}_3 \longrightarrow 2\text{Pb}(\text{NO}_3)_2 + \text{PbO}_2 + 2\text{H}_2\text{O}$   
 8. (a) Yes (b) Yes (c) No (d) Yes  
 9. (a)  $\text{Pb}_3\text{O}_4$  (b)  $\text{PbO}_2$  (c)  $\text{Pb}(\text{NO}_3)_2$

## Practice Exercise 2

1.  $\text{SnCl}_2 + 2\text{NaOH} \longrightarrow (\text{A})$  (white ppt)  $\xrightarrow{\text{NaOH (excess)}} (\text{B})$   
 Identify (A) and (B).  
 2.  $\text{FeCl}_3$  can be reduced to  $\text{FeCl}_2$  by  $\text{SnCl}_2$  as well as by the addition of  $\text{Sn}$  into it. Explain.  
 3.  $\text{FeCl}_3$  gives blood red colour with  $\text{NH}_4\text{CNS}$ . But after  $\text{FeCl}_3$  has been treated with  $\text{SnCl}_2$ , there is no colour with  $\text{NH}_4\text{CNS}$ . Explain.  
 4. Identify (A) and (B) based on following results:  
 Colourless salt (A) + dil.  $\text{HCl} \longrightarrow$  white ppt (B) soluble in hot water.  
 In this reaction vinegar smell is also observed.

5. You are given a colourless solution and was told to add a little  $\text{NaCl}$  solution to it. A cloudy white precipitate was made. What conclusion should you draw about the nature of the colourless solution?  
 6. If you were to attempt to dissolve lead (II) oxide in acid, which acid would you choose?  
 7. Explain why the reactions with  $\text{HCl}$  and  $\text{SO}_2$  show the oxidising nature of  $\text{PbO}_2$ ?  
 8. Predict the result of reacting  $\text{Pb}_3\text{O}_4$  with conc.  $\text{HCl}$ .

### Answers

1. (A) :  $\text{Sn}(\text{OH})_2$  (B) :  $\text{Na}_2\text{SnO}_2$  (sodium stannite)  
 2.  $2\text{FeCl}_3 + \text{SnCl}_2 \longrightarrow \text{SnCl}_4 + 2\text{FeCl}_2$   
 This reaction is possible since  $\text{Sn}^{4+}$  is more stable than  $\text{Sn}^{2+}$  (inert-pair effect)  
 Also  $\text{FeCl}_3$  solution is acidic due to hydrolysis :  

$$\text{FeCl}_3 + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + 3\text{HCl}$$
  
 $\text{Sn}$  added reacts with  $\text{HCl}$  forming nascent hydrogen that can reduce  $\text{FeCl}_3$  to  $\text{FeCl}_2$  :  

$$2\text{HCl} + \text{Sn} \longrightarrow \text{SnCl}_2 + 2\text{H}_{(\text{nascent})}$$
  

$$\text{FeCl}_3 + \text{H} \longrightarrow \text{FeCl}_2 + \text{HCl}$$
  
 3.  $\text{SnCl}_2$  reduces  $\text{FeCl}_3$  to  $\text{FeCl}_2$  hence no colour with  $\text{NH}_4\text{CNS}$ .

4. (A) :  $\text{Pb}(\text{CH}_3\text{COO})_2$  (B) :  $\text{PbCl}_2$   
 5. White ppt can be of  $\text{AgCl}$  or  $\text{PbCl}_2$ . To make further distinction, warm the solution.  $\text{PbCl}_2$  dissolves in hot water while  $\text{AgCl}$  remains insoluble.  $\text{AgCl}$  dissolves in aq  $\text{NH}_3$ .  
 6.  $\text{HNO}_3$  (since  $\text{PbCl}_2$  and  $\text{PbSO}_4$  formed by using  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ , are insoluble).  
 7. The lead changes from  $\text{Pb}(\text{IV})$  to  $\text{Pb}(\text{II})$ ; this represents gain of electrons, i.e., reduction hence  $\text{PbO}_2$  is an oxidising agent. Also stability of  $\text{Pb}^{2+} > \text{Pb}^{4+}$ , hence the reaction  

$$\text{Pb}^{4+} + 2\text{e}^- \longrightarrow \text{Pb}^{2+}$$
  
 is spontaneous in forward side.  
 8.  $\text{Pb}_3\text{O}_4 + 8\text{HCl} \longrightarrow \text{PbCl}_2 + 4\text{H}_2\text{O} + \text{Cl}_2$

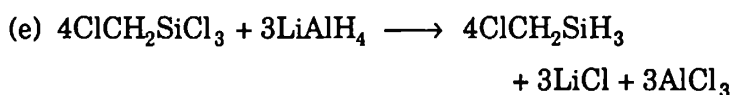
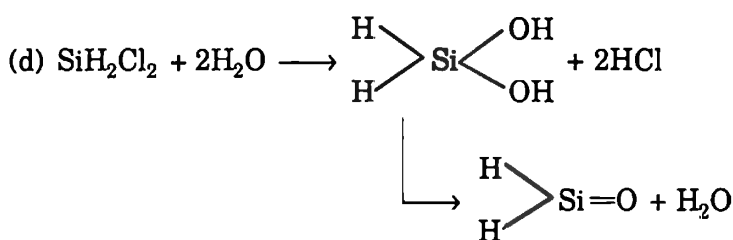
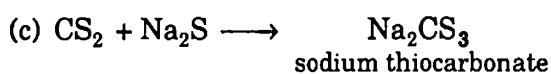
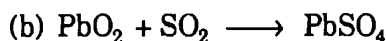
# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** What would you expect to happen when:

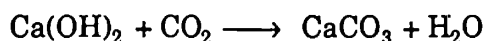
- Tin is heated with a concentrated aqueous solution of sodium hydroxide.
- Sulphur dioxide is passed over lead dioxide.
- Carbon disulphide is shaken with aqueous sodium sulphide.
- Dichlorosilane is hydrolysed by water.
- 4 moles of  $\text{ClCH}_2\text{SiCl}_3$  react with 3 moles of  $\text{LiAlH}_4$  in diethyl ether solution?

**Solution** (a)  $\text{Sn} + 2\text{OH}^- + 4\text{H}_2\text{O} \longrightarrow [\text{Sn}(\text{OH})_6]^{2-} + 2\text{H}_2$



**Problem 2.** If you had a mixture of CO and  $\text{CO}_2$ , how would you find out relative proportions of the two gases in the mixture?

**Solution Method I :** Mixture of CO and  $\text{CO}_2$  is run into  $\text{Ca}(\text{OH})_2$  solution.  $\text{CO}_2$  is absorbed by  $\text{Ca}(\text{OH})_2$  and thus residual volume will be that of CO.



**Method II :** Mixture of CO and  $\text{CO}_2$  is passed over heated charcoal :



Increase in volume will be due to  $\text{CO}_2$ . By measuring total volume after passing over heated charcoal, composition of mixture of CO and  $\text{CO}_2$  can be determined.

**Problem 3.** A mixture of  $\text{CS}_2$  vapour and nitrogen monoxide, NO, gives a vivid blue flame when ignited. A yellow solid is left afterwards. Predict the products of the reaction, and write the equations.

**Solution** You should have predicted that a yellow solid is sulphur formed by oxidation of  $\text{CS}_2$  and thus NO is reduced to  $\text{N}_2$  which appears as a vivid blue flame :



**Problem 4.** CO and  $\text{CN}^-$  ions are highly poisonous. A sign that someone has been poisoned by either of these two chemicals is that the person's blood changes colour. They both have the effect of preventing oxygen being taken up by the blood stream. What might happen to haemoglobin to stop oxygen being taken up?

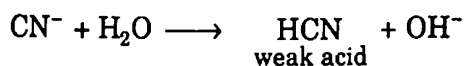
**Solution** CO and  $\text{CN}^-$  ions are able to bond more strongly to the iron atom in haemoglobin than can oxygen. If you were to breathe in CO for any length of time, your haemoglobin would become saturated with CO molecules rather than oxygen. As a result, all the body processes that rely on a supply of oxygen gradually cease. Death is the result.

**Problem 5.** Comment on each of the following observations:

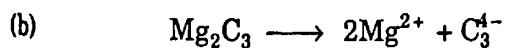
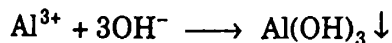
- When an aqueous solution of potassium cyanide is added to aluminium sulphate,  $\text{Al}(\text{OH})_3$  is precipitated.
- The carbide  $\text{Mg}_2\text{C}_3$  liberated propyne ( $\text{CH}_3\text{C}\equiv\text{CH}$ ) on treatment with water.
- Magnesium silicide reacts with ammonium bromide in liquid ammonia to form silane.

(d)  $\text{Me}_2\text{Si} \begin{array}{c} \diagup \text{SiMe}_2 \\ \diagdown \text{SiMe}_2 \end{array} \text{Si} \begin{array}{c} \diagup \text{Me} \\ \diagdown \text{H} \end{array}$  is hydrolysed by aqueous alkali at the same rate as the corresponding Si-D compound.

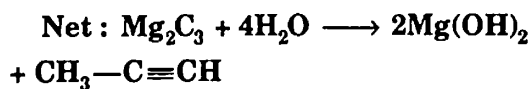
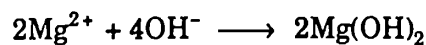
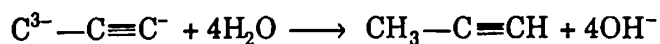
**Solution** (a) Aqueous solution of KCN is alkaline due to hydrolysis of  $\text{CN}^-$  ion.



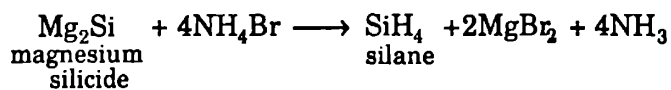
$\text{OH}^-$  formed causes precipitation of  $\text{Al}_2(\text{SO}_4)_3$  as  $\text{Al}(\text{OH})_3$



$\text{C}_3^{4-}$  ion is decomposed by  $\text{H}_2\text{O}$  giving  $\text{CH}_3\text{C}\equiv\text{CH}$



(c) Solutions of  $\text{NH}_4\text{Br}$  (in general ammonium halide) in  $\text{NH}_3$  may be used as acids and  $\text{SiH}_4$  (silane) is formed when  $\text{NH}_4\text{Br}$  in  $\text{NH}_3$  reacts with  $\text{Mg}_2\text{Si}$  (magnesium silicide)



(d) Si—H or Si—D bond is not broken in rate determining step, it is probable that there is attack of  $\text{OH}^-$  on Si.



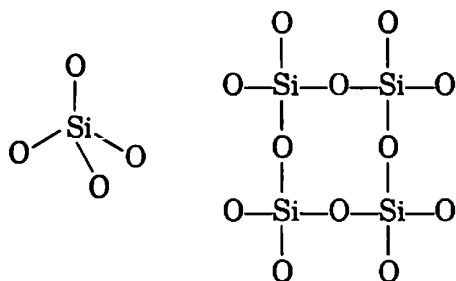
## Explanation

### (a) $\text{CO}_2$ is a gas but $\text{SiO}_2$ is a solid

- Carbon and silicon (Group 14, IVA) have four valence electrons. We might expect carbon and silicon to form oxides with similar properties. In  $\text{CO}_2$  the ability of C and O atoms to form  $\pi$  bonds through the side-wise overlap of their  $2p$  orbitals is strong. The result is strong C=O double bonds and a very stable triatomic molecule.

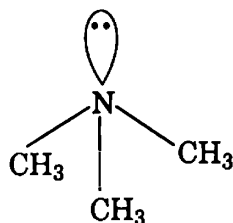


Silicon, being in third period, would have to use  $3p$  orbitals to form double bonds with oxygen. The side-wise overlap of these orbitals with the  $2p$  orbitals of oxygen is too limited for  $\pi$  bond formation. From an energy stand point, a stronger bonding arrangement results if the Si atoms form four single bonds with O atoms (bond energy : 464 kJ/mol) rather than two double bonds (bond energy : 640 kJ/mol) since each O atom must be simultaneously bonded to two Si atoms, the result is a network of  $\text{—Si—O—Si—}$  bonds and thus a hard (giant) solid :



### (b) $(\text{SiH}_3)_3\text{N}$ is planar while $(\text{CH}_3)_3\text{N}$ is pyramidal

- In case of  $(\text{CH}_3)_3\text{N}$ , lone pair on N and three covalent bonds with  $\text{CH}_3$  groups results in  $sp^3$  hybridisation but lone pair-bond pair repulsion causes distortion hence gives pyramidal structure :

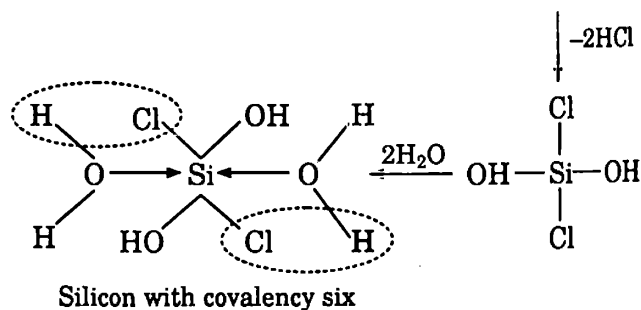
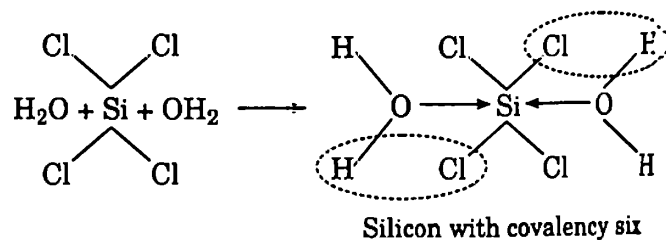
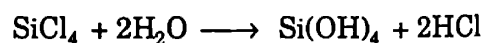


But in case of  $(\text{SiH}_3)_3\text{N}$ , lone pair on the nitrogen is transferred to the empty  $d$ -orbitals of silicon ( $p\pi-d\pi$  overlap) thereby causing planarity of unit.

### (c) $\text{SiCl}_4$ is hydrolysed but $\text{CCl}_4$ is inert to hydrolysis

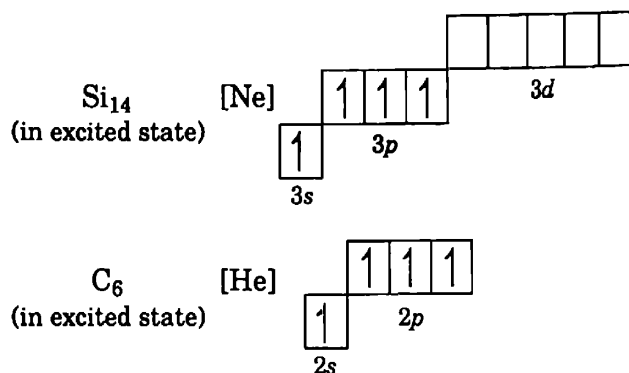
- $\text{SiCl}_4$  and  $\text{CCl}_4$  are covalent compounds. Carbon has maximum covalency of four while silicon has six.

Thus  $\text{CCl}_4$  is inert towards water and is not hydrolysed but  $\text{SiCl}_4$  can coordinate with 2 moles of  $\text{H}_2\text{O}$  molecules and is thus readily hydrolysed :



### (d) Glass made of $\text{SiO}_2$ is attacked by HF with the formation of $\text{SiF}_6^{2-}$ anion. The analogous $\text{CF}_6^{2-}$ does not exist :

- Silicon has  $3d$ -orbitals and can use octahedral  $sp^3d^2$ -hybrid orbitals to bond to six  $\text{F}^-$  ions. Carbon lacks  $2d$ -orbitals ( $2d$  does not exist) and with just  $2s$  and  $2p$  valence orbitals, carbon can form maximum of only four bonds.



### (e) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ readily loses 1 molecule of $\text{H}_2\text{O}$ at $80^\circ\text{C}$ .

- Pyramidal  $\text{SnCl}_2 \cdot \text{H}_2\text{O}$  molecule has a lone pair on Sn. The other  $\text{H}_2\text{O}$ , hydrogen-bonded to the coordinated  $\text{H}_2\text{O}$  is easily lost.

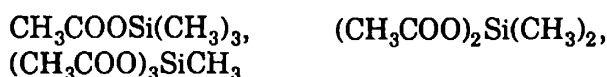
# Master Exercises

## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

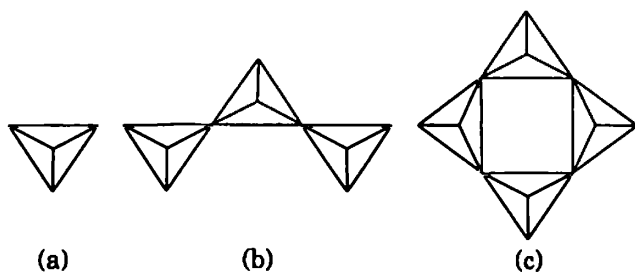
- Carbon has coordination number (C.N.) of four while other elements of this group have C.N. of six. Explain.
- Identify the group 14A element that best fits each of the following descriptions:
  - prefers the +2 oxidation state
  - forms the strongest  $\pi$  bonds
  - is the second most abundant element in the earth's crust
  - forms the most acidic oxide
- Give the formula of a compound in which carbon exhibits an oxidation state of:
  - +4
  - +2
  - 4
- List three properties of diamond, and account for them in terms of structure and bonding.
- Identify (A), (B), (C), (D) and (E) :
 
$$\begin{array}{c} \text{(a) Si} \xrightarrow[\text{conc, } \Delta]{\text{HNO}_3/\text{HF}} \text{(A)} \xrightarrow{\text{HF}} \text{(B)} \\ \quad \quad \quad \downarrow \text{H}_2\text{O} \\ \quad \quad \quad \text{(B) + (C)} \end{array}$$
  - Graphite  $\xrightarrow{\text{hot conc HNO}_3}$  (D)
  - $\text{Na}_2\text{CO}_3 + \text{Si} \xrightarrow{\text{fused}} \text{(E)}$
- Solution of  $\text{CO}_3^{2-}$  (say  $\text{Na}_2\text{CO}_3$ ) is alkaline. Explain.
- Explain why a solution containing  $\text{Ca}^{2+}(\text{aq})$  and  $\text{HCO}_3^-(\text{aq})$  ions is said to be hard?
- What happens if solution of  $\text{Na}_2\text{CO}_3$  is heated with Al?
- A mixture of  $\text{CS}_2$  vapour and nitrogen monoxide, NO, gives a vivid blue flame when ignited. A yellow solid is left afterwards. Predict the products of reaction, and write the equation.
- A student placed a pellet of NaOH on a watch glass. A few days later, she noticed that the pellet was covered with a white solid. What is the identity of this solid?
- List three commercial uses for  $\text{CO}_2$ , and relate each use to one of carbon dioxide's properties.
- Is it wise to write
 
$$\text{Al}_2\text{C}_3 \longrightarrow 4\text{Al}^{3+} + 3\text{C}^{4-} ?$$
- Draw a Lewis structure for the  $\text{C}_2^{2-}$  and  $\text{C}_3^{3-}$  ions.
- Why are CO and  $\text{CN}^-$  harmful?
- Give an example of an ionic carbide. What is the oxidation state of carbon in this compound?
- Which of the following is a more effective greenhouse gas CO or  $\text{H}_2\text{O}$ ?
- Instead of monitoring carbon dioxide, suggest another gas that scientists could study to substantiate the fact that  $\text{CO}_2$  concentration is steadily increasing in the atmosphere.
- The equilibrium constant ( $K_p$ ) for the reaction
 
$$2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}_2(\text{g})$$
 is  $1.4 \times 10^{90}$  at  $25^\circ\text{C}$ . Given this enormous value, why doesn't CO convert totally to  $\text{CO}_2$  in the troposphere?
- What is glanzkohlenstoff?
- Talc,  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$  is the softest material. It has a smooth, greasy touch. It is used in talcum powder. Muscovite,  $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ , is one of the micas, which split into thin layers extremely easily. Both minerals have layer structures. What type of force holds the layers together?
- Silica will react in a similar way with metal sulphates (and phosphates) as it does with carbonates, giving a solid residue and a gas. 1 mole of silica reacts with 1 mole of sodium sulphate,  $\text{Na}_2\text{SO}_4$ . Write the equation.
- What would be the structure of the silicone molecule made from  $\text{Si}(\text{CH}_3)_3\text{Cl}$ ?
- One type of silicone adhesive uses a polymer that has two OH groups left on the ends of the chain :
 
$$\text{HO}-\text{Si}(\text{CH}_3)_2[\text{O}-\text{Si}(\text{CH}_3)_2]_n-\text{O}-\text{Si}(\text{CH}_3)_2-\text{OH}$$

It has been found that this kind of polymer reacts easily with an organo-silicon molecule that contains acetate ( $\text{CH}_3\text{COO}$ ) group. Which of these three molecules

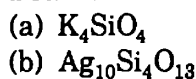


would you choose to add to the hydroxy polymer in order to make a strong adhesive?

24. The following pictures represent various silicate anions. Give the formula and charge of each anions.



25. Draw the structure of the silicate anion in :



26. A colourless solution (X) gives black ppt (Y) on passing  $\text{H}_2\text{S}$  gas. (X) also gives white ppt (Z) with  $\text{SnCl}_2$ . (Z) changes to grey. Identify (X), (Y) and (Z).

27. One problem with making crystals of tin (II) chloride is that they are easily hydrolysed by warm water. Instead of dissolving tin in  $\text{HCl}(\text{aq})$  how else might the anhydrous chloride be made?

28.  $\text{HF}$  can't be stored in a glass vessel. Explain.

29. Fill in the blanks :

- (a) Glass is a ..... liquid.  
(b) Markings on the glass plate are made by use of .....  
(c) Glass with high refractive index contains .....  
(d) Pyrex glass can withstand heat and contains .....  
(e) Opal glass contains .....

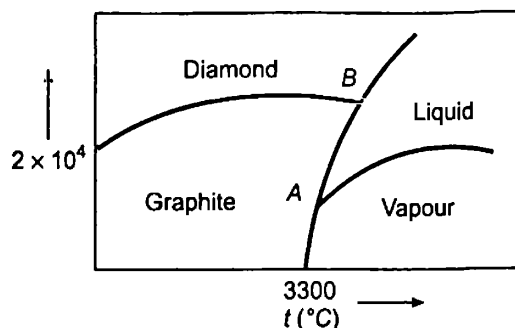
## Analytical Questions

1. Explain :

- (i) Why silicon is not expected to form an allotrope with graphite like structure?  
(ii) Contrary to  $(\text{CH}_3)_2\text{O}$ ,  $(\text{SiH}_3)_2\text{O}$  does not form addition compound with  $\text{BF}_3$ .

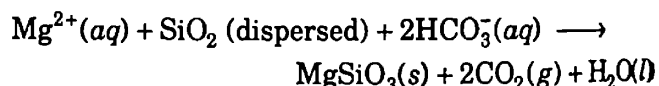
2. Given below the phase diagram of carbon, answer the following questions:

- (a) How many triple points are there and what are the phases that can coexist at each triple point?  
(b) Which has a higher density, graphite or diamond?



- (c) Synthetic diamond can be made from graphite. Using the phase diagram, how would you go about making diamond?

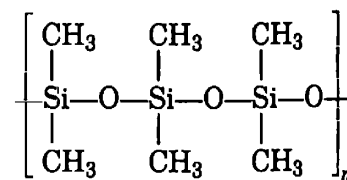
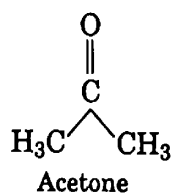
3. Consider the following list of elements: C, Se, B, Sn, Cl. Identify the element on this list that  
(a) has the largest atomic radius,  
(b) is the most electronegative,  
(c) is the best electrical conductor,  
(d) has a maximum oxidation state of +6,  
(e) forms a hydride with the empirical formula  $\text{XH}_3$
4. Carbon is an essential element in the molecule on which life is based. Would silicon be equally satisfactory? Explain.
5. The name dilead(II) lead(IV) oxide and plumbous orthoplumbate have both been used to describe red lead,  $\text{Pb}_3\text{O}_4$ . Show that these names are consistent with this mixed oxide.
6. Write chemical equations to represent the following reactions:  
(a) The dissolving of  $\text{PbO}$  in  $\text{NaOH}(\text{aq})$ .  
(b) The disproportionation of  $\text{SnO}$  to  $\text{Sn}$  and  $\text{SnO}_2$ .  
(c) The oxidation of  $\text{HCl}(\text{aq})$  to  $\text{Cl}_2(\text{g})$  by  $\text{PbO}_2(\text{s})$ .  
(d) The production of basic lead carbonate (white lead)  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  by the action of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  on  $\text{PbO}$ .
7. One natural source of atmospheric  $\text{CO}_2$  is precipitation reaction such as the precipitation of silicates in the oceans :



How many grams of magnesium silicate would be precipitated during the formation of 100 L of  $\text{CO}_2$  at  $30^\circ\text{C}$  and 775 Torr?

$$(\text{Mg} = 24, \text{Si} = 28, \text{C} = 12, \text{O} = 16)$$

8. The organic solvent acetone has the molecular formula  $(\text{CH}_3)_2\text{CO}$ . The silicon analogue, a thermally stable lubricant, is a polymer,  $[(\text{CH}_3)_2\text{SiO}]_n$ . Account for the difference in structure.



## NCERT Problems

- Write balanced equations for the following reactions.
  - Combustion of  $C_4H_{10}$  in a limited supply of oxygen to form carbon monoxide and water.
  - The reaction of calcium carbide with water to form acetylene.
  - The preparation of calcium cyanamide from calcium carbide and nitrogen.
  - Formation of hydrogen cyanide from methane and ammonia.
- Write resonance structures for  $CO_3^{2-}$  and  $HCO_3^-$ .

- What is the oxidation state of carbon in each of the following compounds?
 

|               |             |
|---------------|-------------|
| (a) CO        | (b) HCN     |
| (c) $H_2CO_3$ | (d) $CaC_2$ |
- What is dry ice? Why is it so called?
- What is the state of hybridisation of carbon in
 

|                 |              |
|-----------------|--------------|
| (a) $CO_3^{2-}$ | (b) HCN      |
| (c) diamond     | (d) graphite |
- Explain the differences in the properties of diamond and graphite on the basis of their structures.
- What are fullerenes? How are they prepared?

## Exercise 2

## (Stage 2 : High Skill Problem Solving)

## Only One Option Correct

- Stability of hydrides of carbon family is in order
  - $CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$
  - $CH_4 < SiH_4 < GeH_4 < SnH_4 < PbH_4$
  - $CH_4 > SnH_4 > GeH_4 > SiH_4 > PbH_4$
  - None of the above
- Select correct statement.
  - oxides of carbon family ( $MO_2$ ) are all network solids with octahedral coordination
  - Silicon dioxide (silica) is a network solid with tetrahedral coordination and is a giant molecule
  - $GeO_2$ ,  $SnO_2$  and  $PbO_2$  are all acidic oxides
  - None of the above appears correct
- Dry ice is
 

|               |               |
|---------------|---------------|
| (a) $H_2O(s)$ | (b) $NH_3(g)$ |
| (c) $CO_2(s)$ | (d) $PH_3(g)$ |
- Select correct statements.
  - Hydrides of B and Si are volatile and catch fire on exposure to air
  - Oxides of B and Si ( $B_2O_3$  and  $SiO_2$ ) are acidic in nature
  - Borates and silicates have tetrahedral  $BO_4$  and  $SiO_4$  structural units
  - All the above are correct statements
- Select correct statements.
  - Catenation is maximum in carbon
  - Carbon has pronounced ability to form  $p\pi-p\pi$  multiple bonds to itself and to other elements like O and N
  - Both (a) and (b) are correct
  - None of the above is correct
- Consider following statements,
 

I: In diamond, each carbon atom is linked tetrahedrally to four other carbon atoms by  $sp^3$  bonds.

II: Graphite has planar hexagonal layers of carbon atoms held together by weak van der Waals' forces.

III: Silicon exists only in diamond structure due to its tendency to form  $p\pi-p\pi$  bonds to itself.

In this

- Only I and II are correct
- Only I is correct
- Only II and III are correct
- All the above are correct statement

7. Out of  $CO_2$ ,  $SiO_2$ ,  $GeO_2$ ,  $SnO_2$  and  $PbO_2$

- $CO_2$  and  $SiO_2$  are acidic,  $SnO_2$  is amphoteric and  $PbO_2$  is an oxidising agent
- $PbO_2$  is converted to  $Pb(NO_3)_2$  on reaction with  $HNO_3$
- both (a) and (b) are correct
- none of the above is correct

8. Which is incorrect statement about silicones?

- They are repeating units ( $SiO_4$ ) in silicates
- They are synthetic polymers containing repeated  $R_2SiO_2$  units
- They are formed by hydrolysis of  $R_2SiCl_2$
- All the above are incorrect statements

9. Which one of the following bonds has the highest bond energy?

- |           |           |
|-----------|-----------|
| (a) C—C   | (b) Si—Si |
| (c) Ge—Ge | (d) Sn—Sn |

10. Which of the following species have undistorted octahedral structures?

- |                 |             |
|-----------------|-------------|
| 1. $SF_6$       | 2. $PF_6^-$ |
| 3. $SiF_6^{2-}$ | 4. $SeF_6$  |

Select the correct answer using the codes given below

- |                |                |
|----------------|----------------|
| (a) 2, 3 and 4 | (b) 1, 3 and 4 |
| (c) 1, 2 and 3 | (d) 1, 2 and 4 |

11. Which of the following statements are true for zeolites?

1. They are formed by the replacement of some of the silicon atoms of the  $\text{SiO}_2$  lattice, by say, aluminium.
2. They have a more closed structure than feldspar.
3. They can absorb  $\text{CO}_2$ ,  $\text{NH}_3$  and  $\text{EtOH}$ .
4. They can separate straight chain hydrocarbons from a mixture containing both straight, chain and branched chain hydrocarbons.

Of these statements

- (a) 1, 2 and 3 are correct (b) 1, 3 and 4 are correct  
(c) 1, 2 and 4 are correct (d) 2, 3 and 4 are correct

12. Artificial gem used for cutting glass is

- (a) graphite (b) diamond  
(c)  $\text{SiC}$  (d)  $\text{CaCN}_2$

13. Red lead used as primer for iron to prevent it from rusting is

- (a)  $\text{Pb}_3\text{O}_4$  (b)  $\text{PbO}$   
(c)  $\text{PbO}_2$  (d)  $\text{Pb}_2\text{O}$

14. Lead as impurity in the extraction of silver is removed by

- (a) Parke's process (b) Solvay process  
(c) Cyanide process (d) None of these

15. Which involves breaking of covalent bonds?

- (a) Boiling of  $\text{H}_2\text{S}$  (b) Melting of  $\text{SiO}_2$   
(c) Melting of  $\text{KCN}$  (d) Boiling of  $\text{CCl}_4$

16. Which is silane?

- (a)  $\text{SiO}_2$  (b)  $\text{SiO}_3$   
(c)  $\text{SiH}_4$  (d)  $\text{Si}$

17. Holme's signals can be given by using

- (a)  $\text{CaC}_2 + \text{CaCN}_2$  (b)  $\text{CaC}_2 + \text{Ca}_3\text{P}_2$   
(c)  $\text{CaC}_2 + \text{CaCO}_3$  (d)  $\text{Ca}_3\text{P}_2 + \text{CaCN}_2$

18. Which is/are true statements?

- (a) Diamond is unaffected by conc acids but graphite reacts with hot conc.  $\text{HNO}_3$  forming mellitic acid,  $\text{C}_6(\text{COOH})_6$   
(b)  $\text{CO}$  is toxic because it forms a complex with haemoglobin in the blood  
(c)  $\text{C}_3\text{O}_2$ , carbon suboxide, is a foul-smelling gas  
(d) All the above are true statements

19. Carborundum is

- (a)  $\text{CaC}_2$  (b)  $\text{Fe}_3\text{C}$   
(c)  $\text{CaCO}_3$  (d)  $\text{SiC}$

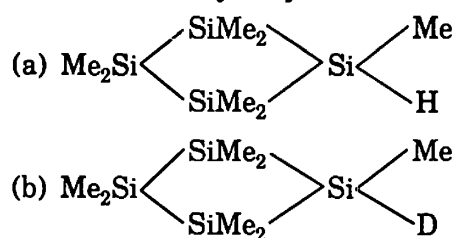
20. Gas that strikes in thundering of light is

- (a)  $\text{CO}$  (b)  $\text{NO}$   
(c)  $\text{CO}_2$  (d)  $\text{H}_2$

21.  $\text{NO}_2$  is not obtained when following is heated

- (a)  $\text{Pb}(\text{NO}_3)_2$  (b)  $\text{AgNO}_3$   
(c)  $\text{LiNO}_3$  (d)  $\text{KNO}_3$

22. In which case hydrolysis is faster



- (c) at equal rate  
(d) no hydrolysis

23. Which of the following is the ionic carbide?

- (a)  $\text{Fe}_3\text{C}$  (b)  $\text{SiC}$   
(c)  $\text{CaC}_2$  (d)  $\text{Cu}_2\text{C}$

24. The silicate anion in the mineral kinoite is a chain of three  $\text{SiO}_4$  tetrahedra that share corners with adjacent tetrahedra. The mineral also contains  $\text{Ca}^{2+}$  ions,  $\text{Cu}^{2+}$  ions, and water molecules in a 1:1:1 ratio. The mineral is

- (a)  $\text{Ca}_2\text{Cu}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$   
(b)  $\text{CaCuSi}_3\text{O}_{10} \cdot \text{H}_2\text{O}$   
(c)  $\text{Ca}_2\text{Cu}_2\text{Si}_3\text{O}_8 \cdot 2\text{H}_2\text{O}$   
(d)  $\text{Ca}_2\text{Cu}_2\text{Si}_3\text{O}_6 \cdot 2\text{H}_2\text{O}$

25. The best oxidising agent of the following oxides is

- (a)  $\text{SnO}_2$  (b)  $\text{PbO}_2$   
(c)  $\text{HgO}$  (d)  $\text{MgO}$

26. Dipole moment of  $\text{CO}$  is very small (0.1 D) (inspite of the larger difference in electronegativity between C and O) and negative end of the dipole lies near the less electronegative C-atom. It is due to

- (a) occupation of anti-bonding molecular orbitals  
(b) occupation of empty  $d$ -orbitals  
(c) occupation of lone-pairs  
(d) occupation of the lone pairs as well as empty  $d$ -orbitals

27. Carbon and silicon belong to (IV) group. The maximum coordination of carbon is commonly occurring compounds is 4, whereas that of silicon is 6. This is due to

- (a) large size of silicon  
(b) more electropositive nature of silicon  
(c) availability of  $d$ -orbital in silicon  
(d) both (a) and (b)

28. In graphite, additional electrons are

- (a) localised on each C-atom  
(b) localised on every third C-atom  
(c) present in anti-bonding orbital  
(d) delocalised forming extended  $\pi$ -bonding system

29.  $\text{PbO}_2 \longrightarrow \text{PbO} \quad \Delta G_{298} < 0$

$\text{SnO}_2 \longrightarrow \text{SnO} \quad \Delta G_{298} > 0$

Most probable oxidation state of Pb and Sn will be

- (a)  $\text{Pb}^{4+}, \text{Sn}^{4+}$  (b)  $\text{Pb}^{4+}, \text{Sn}^{2+}$   
(c)  $\text{Pb}^{2+}, \text{Sn}^{2+}$  (d)  $\text{Pb}^{2+}, \text{Sn}^{4+}$

30. When vapours of  $\text{SiCl}_4$  are passed over hot Mg, then the product formed is  
 (a)  $\text{SiCl}_2 + \text{MgCl}_2$  (b)  $\text{MgSi} + \text{Cl}_2$   
 (c)  $\text{MgSiCl}_6$  (d)  $\text{Si} + \text{MgCl}_2$
31. Which one of the following is not a green house gas?  
 (a)  $\text{CO}_2$  (b)  $\text{H}_2\text{O}$   
 (c)  $\text{N}_2$  (d)  $\text{O}_3$
32. Which of the following has the highest calorific value?  
 (a) Water gas (b) Producer gas  
 (c) Carbonium oxide (d) Coal gas
33. Carbogen is  
 (a) mixture of  $\text{CO} + \text{CO}_2$   
 (b) mixture of  $\text{O}_2 + \text{CO}_2$   
 (c) pure form of carbon  
 (d) unsaturated organic compound
34. Carbon monoxide is a poisonous gas, the antidote used for this poisoning is  
 (a) pure oxygen (b) carbonic acid  
 (c) carborundum (d) carbogen
35. Method used for obtaining highly pure silicon, used as a semiconductor material, is  
 (a) oxidation (b) electrochemical  
 (c) crystallisation (d) zone refining
36. Carbon and silicon belong to group 14. What is nature of carbide of silicon?  
 (a) Covalent (b) Ionic  
 (c) Interstitial (d) None of these
37. Which of the following shows electrical conduction?  
 (a) Potassium ion (b) Graphite  
 (c) Diamond (d) Sodium ion
38. Water glass is  
 (a) Glass made up of water  
 (b) Sodium silicate  
 (c) Water gas  
 (d) Crystal carbonate
39. Name of the structure of silicates in which three oxygen atoms of  $[\text{SiO}_4]^{4-}$  are shared is  
 (a) pyrosilicate  
 (b) sheet silicate  
 (c) linear chain silicate  
 (d) three dimensional silicate
40. Marsh gas primarily contains  
 (a)  $\text{CH}_4$  (b)  $\text{C}_2\text{H}_6$   
 (c)  $\text{H}_2\text{S}$  (d)  $\text{C}_2\text{H}_2$
41. Litharge is chemically  
 (a)  $\text{PbO}$  (b)  $\text{PbO}_2$   
 (c)  $\text{Pb}_3\text{O}_4$  (d)  $(\text{CH}_3\text{COO})_2\text{Pb}$
42. The gas evolved by heating potassium ferrocyanide crystals with conc.  $\text{H}_2\text{SO}_4$  is  
 (a)  $\text{CO}$  (b)  $\text{CO}_2$   
 (c)  $\text{SO}_2$  (d)  $\text{SO}_3$
43. Graphite is a good conductor of heat and electricity because it contains  
 (a) layers of carbon atoms  
 (b) sheet like structure  
 (c) free electrons  
 (d)  $p\pi-d\pi$  bonding
44.  $(\text{Me}_2)_2\text{SiCl}_2$  on hydrolysis will produce  
 (a)  $(\text{Me})_2\text{Si}(\text{OH})_2$  (b)  $(\text{Me})_2\text{Si}=\text{O}$   
 (c)  $[-\text{O}-(\text{Me})_2\text{Si}-\text{O}-]_n$  (d)  $\text{Me}_2\text{SiCl}(\text{OH})$
45. I.  $\text{PbO}_2 \longrightarrow \text{PbO} \quad \Delta G_{298} < 0$   
 II.  $\text{SnO}_2 \longrightarrow \text{SnO} \quad \Delta G_{298} > 0$   
 Which of the above is/are true?  
 (a) I (b) II  
 (c) Both (a) & (b) (d) None of these
46. Which one of the following statements about the zeolite is false?  
 (a) They are used as cation exchangers  
 (b) They have open structure which enables them to take up small molecules  
 (c) Zeolites are aluminosilicates having three dimensional network  
 (d) Some of the  $\text{SiO}_4^{4-}$  units are replaced by  $\text{AlO}_4^{5-}$  and  $\text{AlO}_6^{9-}$  ions in zeolites
47. Bonding present between the carbon atoms in graphite is  
 (a) metallic (b) ionic  
 (c) covalent (d) van der Waals' forces
48. Which of the following cuts ultraviolet rays?  
 (a) Soda glass (b) Crooke's glass  
 (c) Pyrex (d) None of these
49. In diamond crystal each carbon atom is linked with carbon atoms. The number of carbon atoms linked is  
 (a) 2 (b) 4  
 (c) 3 (d) 1
50. Which of the following has the highest first ionisation energy?  
 (a) Lithium (b) Beryllium  
 (c) Boron (d) Carbon
51. Which gas is used in aerated water?  
 (a)  $\text{CO}_2$  (b)  $\text{SO}_2$   
 (c)  $\text{CO}$  (d) Water vapours
52. In which of the following the angle between the two covalent bond is maximum?  
 (a)  $\text{H}_2\text{O}$  (b)  $\text{CO}_2$   
 (c)  $\text{CH}_4$  (d)  $\text{NH}_3$
53. Percentage of lead in lead pencil is  
 (a) 30 (b) 20  
 (c) 10 (d) zero
54. Which of the following is not an acid anhydride?  
 (a)  $\text{CO}_2$  (b)  $\text{CO}$   
 (c)  $\text{SO}_2$  (d)  $\text{SO}_3$

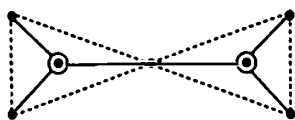
55. The compound having maximum carbon percentage is  
 (a) peat (b) bituminous  
 (c) lignite (d) anthracite
56. At room temperature the solid compound is  
 (a)  $\text{CO}_2$  (b)  $\text{SiO}_2$   
 (c)  $\text{NO}_2$  (d)  $\text{SO}_2$
57. By passing air over red hot coke the gas obtained is  
 (a) coal gas (b) water gas  
 (c) oil gas (d) producer gas
58. White lead is  
 (a)  $\text{PbSO}_4 \cdot \text{PbO}$  (b)  $\text{PbCO}_3 \cdot \text{PbO}$   
 (c)  $\text{PbCO}_3$  (d)  $\text{Pb(OH)}_2 \cdot \text{PbCO}_3$
59. Silicon is an important constituent of  
 (a) rocks (b) amalgams  
 (c) chlorophyll (d) haemoglobin
60. When chlorine is passed through molten tin, the product obtained is  
 (a)  $\text{SnCl}_4$  (b)  $[\text{SnCl}_6]^{2-}$   
 (c)  $[\text{SnCl}_4]^{2-}$  (d)  $\text{SnCl}_2$
61. In making casting of metal, silicon is used as  
 (a) oxidiser (b) semiconductor  
 (c) deoxidiser (d) None of these
62. Sindoor is represented by  
 (a)  $\text{Pb(NO}_3)_2$  (b)  $\text{PbCO}_3 \cdot \text{Pb(OH)}_2$   
 (c)  $\text{Pb(OH)}_2 \cdot 4\text{PbCO}_3$  (d)  $\text{Pb}_3\text{O}_4$
63. Lead is soluble in  
 (a)  $\text{CH}_3\text{COOH}$  (b)  $\text{H}_2\text{SO}_4$   
 (c)  $\text{HCl}$  (d)  $\text{HNO}_3$
64. Quartz is a crystalline variety of  
 (a) silicon carbide (b) sodium silicate  
 (c) silica (d) silicon
65. Which of the following have highest melting points?  
 (a) *p*-block elements (b) *s*-block elements  
 (c) *d*-block elements (d) None of these
66. Which of the following halides is least stable and doubtful existence?  
 (a)  $\text{Cl}_4$  (b)  $\text{SnI}_4$   
 (c)  $\text{GeI}_4$  (d)  $\text{PbI}_4$
67. Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behaviour is that graphite  
 (a) is a non crystalline substance  
 (b) is an allotropic form of diamond  
 (c) has molecules of variable molecular masses like polymers  
 (d) has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interplate bonds
68. The variation in element-element bond energy follows the order  
 (a)  $\text{C—C} > \text{Si—Si} > \text{Ge—Ge} > \text{Sn—Sn} > \text{Pb—Pb}$   
 (b)  $\text{Si—Si} > \text{C—C} > \text{Pb—Pb} > \text{Sn—Sn} > \text{Ge—Ge}$   
 (c)  $\text{C—C} > \text{Ge—Ge} > \text{Sn—Sn} > \text{Pb—Pb} > \text{Si—Si}$   
 (d)  $\text{C—C} > \text{Sn—Sn} > \text{Pb—Pb} > \text{Ge—Ge} > \text{Si—Si}$
69. Thermodynamically most stable form of carbon is  
 (a) graphite (b) diamond  
 (c) ionsdaleite (d) chaoite
70. The crystal structures of both chaoite and carbon (VI) are based on  
 (a)  $\text{—C}\equiv\text{C—C}\equiv\text{C—}$  (b)  $\text{—C}\equiv\text{C—C}\equiv\text{C—}$   
 (c)  $\begin{array}{c} | \quad | \\ \text{—C—C—} \\ | \quad | \end{array}$  (d) all of these
71. Elements of group 14 used in semiconductors are  
 (a) C, Si, Ge (b) Si, Ge, Sn  
 (c) Si, Ge (d) B, Si, Ge
72. Select correct statement about stability of cations.  
 (a)  $\text{Ge}^{4+} > \text{Sn}^{4+} > \text{Pb}^{4+}$   
 (b)  $\text{Ge}^{2+} < \text{Sn}^{2+} < \text{Pb}^{2+}$   
 (c)  $\text{Pb}^{2+} > \text{Pb}^{4+}, \text{Sn}^{4+} > \text{Sn}^{2+}$   
 (d) All the above are correct statements
73. In which case geometry of the molecule is pyramidal?  
 (a)  $\text{N(CH}_3)_3$  (b)  $\text{N(SiH}_3)_3$   
 (c) Both (a) and (b) (d) None of these
74.  $\pi\pi$ - $\pi\pi$  multiple bonds occur between  
 (a) C and C (b) C and O  
 (c) C and N (d) in all cases
75. Buckminster fullerene is  
 (a) pure graphite (b) C-60  
 (c) diamond (d) C-90
76. Lead pencil contains  
 (a) lead  
 (b) graphite  
 (c) alloy of lead and tin  
 (d) alloy of lead and graphite
77. Standard reduction electrode potential of lead suggests that it is reactive metal but it appears more noble (unreactive). It is due to  
 (a) surface coating of oxide  
 (b) high over potential of reduction of  $\text{H}^+$  to  $\text{H}_2$   
 (c) both (a) and (b)  
 (d) None of the above
78. Hot conc.  $\text{HNO}_3$  converts graphite into  
 (a) graphite oxide  
 (b) benzene hexacarboxylic acid  
 (c) both (a) and (b)  
 (d) None of the above
79. Silicon reacts with hot solution of  $\text{NaOH}$  forming  
 (a)  $\text{Si(OH)}_4$  (b)  $\text{Si(OH)}_2$   
 (c)  $\text{SiO}_2$  (d)  $\text{Na}_4\text{SiO}_4$

80. Select incorrect statement.  
 (a) Mellitic acid is benzene hexa-carboxylic acid  
 (b) Pb dissolves in conc. HCl forming  $\text{PbCl}_2$   
 (c) Pb dissolves in hot NaOH forming  $\text{Na}_2[\text{Pb}(\text{OH})_6]$   
 (d) Diamond is unreactive but graphite forms  $(\text{CF})_n$  with  $\text{F}_2$
81. When a mixture of carbon monoxide and chlorine is exposed to sunlight the product formed is  
 (a) thionyl chloride  
 (b) phosgene  
 (c) phosphine  
 (d) carbon tetrachloride
82. Stable oxides of carbon are  
 (a)  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_3\text{O}_2$  (b)  $\text{CO}_2$ ,  $\text{C}_3\text{O}_2$ ,  $\text{C}_2\text{O}$   
 (c)  $\text{CO}$ ,  $\text{CO}_2$  (d)  $\text{C}_2\text{O}$ ,  $\text{C}_3\text{O}_2$
83. CO behaves as  
 (a) Lewis acid (b) Lewis base  
 (c) amphoteric oxide (d) None of these
84. Which reaction takes place during respiration?  
 (a)  $6\text{CO}_2 + 6\text{H}_2\text{O} \longrightarrow 6\text{O}_2 + \text{C}_6\text{H}_{12}\text{O}_6$   
 (b)  $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$   
 (c)  $\text{C} + \frac{1}{2}\text{O}_2 \longrightarrow \text{CO}$   
 (d)  $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \longrightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$
85.  $\text{CO}_2$  in water behaves as  
 (a) weak dibasic acid  $\text{H}_2\text{CO}_3$   
 (b) weak monobasic acid  $\text{HO}-\text{CO}_2\text{H}$   
 (c) weak diacid base  $\text{CO}(\text{OH})_2$   
 (d) weak monoacid base  $\text{HO}-\text{CO}_2\text{H}$
86. A certain compound on burning in air forms three oxides. One of the oxides turned lime water milky, the other turned anhydrous  $\text{CuSO}_4$  blue and third formed a solution of  $\text{pH} = 9$ . Compound is formed of  
 (a) S, N and H (b) S, N and C  
 (c) S, C and H (d) S, H and Na
87. Concentrations of the atmospheric  $\text{CO}_2$  have been rising because of  
 (a) use of fossil fuels (b) acid rain  
 (c) photochemical smog (d) ozone depletion
88. Principal cause of ozone depletion is the  
 (a) presence of fluorocarbons  
 (b) acid rain  
 (c) photochemical smog  
 (d) green-house effect
89. Global warming is called  
 (a) photochemical smog (b) green-house effect  
 (c) acid rain (d) respiration
90. Green house effect is due to  
 (a) disturbance of the earth's delicate thermal balance  
 (b) absorption of heat radiation by atmospheric gases particularly water vapours  
 (c) both (a) and (b)  
 (d) None of the above
91. Methanides are  
 (a)  $\text{Mg}_2\text{C}_3$ ,  $\text{Be}_2\text{C}$ ,  $\text{Al}_4\text{S}_3$  and  $\text{CaC}_2$   
 (b)  $\text{Mg}_2\text{C}_3$ ,  $\text{Be}_2\text{C}$  and  $\text{Al}_4\text{C}_3$   
 (c)  $\text{Be}_2\text{C}$ ,  $\text{Al}_4\text{C}_3$  and  $\text{CaC}_2$   
 (d)  $\text{Be}_2\text{C}$  and  $\text{Al}_4\text{C}_3$
92. Select correct statement(s).  
 (a) Cyanamide ion  $(\text{CN}_2^{2-})$  is isoelectronic with  $\text{CO}_2$  and has the same linear structure  
 (b)  $\text{Mg}_2\text{C}_3$  reacts with water to form propyne  
 (c)  $\text{CaC}_2$  has NaCl type of lattice  
 (d) all the above are correct statements
93. Select incorrect statement(s).  
 (a) Interstitial carbides are formed by metalloids like Si and B  
 (b) Covalent carbides are formed by metalloids  
 (c) CO and  $\text{CN}^-$  both are fatal due to complex formation with Fe(III) present in blood  
 (d) SiC is called carborundum
94. Which is/are used as ligand in complexes?  
 (a)  $\text{CN}^-$  (b) CO  
 (c) Both (a) and (b) (d) None of these
95. Sulphide mineral +  $\text{CN}^- \xrightarrow{\text{O}_2} [\text{M}(\text{CN})_2]^-$   

$$2[\text{M}(\text{CN})_2]^- + \text{Zn} \longrightarrow [\text{Zn}(\text{CN})_4]^{2-} + 2\text{M}$$
  
 M can be  
 (a) Mg, Ag, Au (b) Ag, Au  
 (c) Pt, Au (d) Pt, Ag
96. When zeolite is treated with hard water, there is exchange reaction between calcium/magnesium ion/and .....  
 (a) aluminium ion (b) sodium ion  
 (c) water of hydration (d) sulphate ion
97. Select correct statement(s).  
 (a) Si uses all of its valence electrons in an  $\text{sp}^3$ -hybridisation and crystallises in an fcc structure similar to diamond.  
 (b) Diamond is an electrical insulator, graphite is an electrical conductor but silicon is a semiconductor.  
 (c) Most common silica is quartz.  
 (d) All of the above are correct statements.
98. Silicones are  
 (a) synthetic polymers containing repeated  $\text{R}_2\text{SiO}$  units  
 (b) silicates with common  $\text{SiO}_4$  unit  
 (c) ketones with silyl group  $(\text{SiH}_3)$  similar to alkyl  $(\text{SiH}_3)_2\text{CO}$   
 (d) Zircon (neso silicates)



99. Formula of the following silicate anion is



- (a)  $\text{SiO}_4^{4-}$  (b)  $\text{Si}_2\text{O}_7^{6-}$   
(c)  $\text{Si}_2\text{O}_8^{6-}$  (d)  $\text{Si}_3\text{O}_9^{6-}$

100. The minerals having silicate chains are collectively called

- (a) olivine (b) zircon  
(c) pyroxenes (d) natrolite

101. Glass is best described as a

- (a) solid (b) liquid  
(c) super cooled liquid (d) colloidal sol

102. Which among the following statements is false regarding glass?

- (a) it absorbs ultra-violet light  
(b) it consists of silicates of sodium and alkali  
(c) HF causes marking on glass  
(d) all the halogen acids (HF, HCl, HBr and HI) are stored in glass bottles

103. The colour of blue glass is due to the presence of oxide of

- (a) chromium (b) cobalt  
(c) gold (d) silver

104. Non-oxide ceramics can be

- (a)  $\text{B}_4\text{C}$  (b)  $\text{SiC}$   
(c)  $\text{Si}_3\text{N}_4$  (d) all of these

105. Glass having higher refractive index is prepared using

- (a)  $\text{NiO}$  (b)  $\text{CoO}$   
(c)  $\text{PbO}$  (d)  $\text{CaO}$

106. Amphoteric oxides are

- (a)  $\text{SnO}$ ,  $\text{SnO}_2$  (b)  $\text{GeO}$ ,  $\text{GeO}_2$   
(c) both (a) and (b) (d) None of these

107. Compound used on thermal insulator is

- (a) silica gel (b) zeolites  
(c) silicones (d) asbestos

108.  $\text{SnCl}_4$  can be used as

- (a) reducing agent  
(b) oxidising agent  
(c) catalyst in Friedel Craft's reaction  
(d) a base

109. Aqueous solution of  $\text{SnO}$  liberates  $\text{CO}_2$  with  $\text{NaHCO}_3$ . This shows that  $\text{SnO}$  is

- (a) an acidic oxide  
(b) a basic oxide  
(c) an amphoteric oxide  
(d) a Lewis acid

110. Which silicon compound is used as lubricant?

- (a) Asbestos (b) Silicones  
(c) Zeolite (d) Mica

111. Out of Si, Ge, Sn and Pb which forms stable ionic compounds in divalent state?

- (a) Pb (b) Sn  
(c) Ge (d) Si

112. Select correct statement about  $\text{PbO}$ .

- (a) Red oxide is called litharge  
(b) Yellow oxide is called massicot  
(c) Both (a) and (b) are correct  
(d) None of the above is correct

113.  $\text{Pb}_3\text{O}_4$  reacts with  $\text{HNO}_3$  forming nitrate and oxide which are

- (a)  $\text{Pb}(\text{NO}_3)_4$  from  $\text{PbO}_2$ , and  $\text{PbO}$  remains unreacted  
(b)  $\text{Pb}(\text{NO}_3)_2$  from  $\text{PbO}$ , and  $\text{PbO}_2$  remains unreacted  
(c)  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Pb}(\text{NO}_3)_4$ , and  $\text{PbO}$  remains unreacted  
(d)  $\text{Pb}_3\text{O}_4$  remains insoluble in  $\text{HNO}_3$

114. Unstable lead compounds are

- (a)  $\text{PbCl}_4$ ,  $\text{PbBr}_4$  and  $\text{PbI}_4$  (b)  $\text{PbCl}_2$ ,  $\text{PbBr}_2$  and  $\text{PbI}_2$   
(c)  $\text{PbO}$ ,  $\text{PbO}_2$  and  $\text{Pb}_3\text{O}_4$  (d)  $\text{PbCl}_4^{2-}$ ,  $\text{PbCl}_6^{2-}$

115.  $\text{PbCl}_2$  is soluble in

- (a) dil. HCl (b)  $\text{CH}_3\text{COOH}$   
(c) hot water (d) dil.  $\text{H}_2\text{SO}_4$

## One or More Than One Options Correct

1. Select correct statement(s).

- (a) Graphite is composed of planar, two dimensional sheets of  $sp^2$  hybridised carbon atoms.  
(b) Each sheet is a network of fused, hexagonal rings of carbons.  
(c) The layers in graphite are held together by relatively weak van der Waals forces of attraction.  
(d) Graphite is thermodynamically the most stable allotropic form of carbon.

2. Select correct statement(s).

- (a) In graphite, only three electrons (out of four) are involved in  $\sigma$  bonding.  
(b)  $\pi$ -bonding electrons in graphite are delocalised over the whole structure.  
(c) Conduction of electricity in graphite is due to mobile electrons.  
(d) Diamond is insulator due to absence of mobile electrons.

3. Conc.  $\text{H}_2\text{SO}_4$  reacts with carbon forming

- (a)  $\text{CO}_2$  (b)  $\text{SO}_2$   
(c)  $\text{H}_2\text{CO}_3$  (d)  $\text{H}_2\text{SO}_3$

4. Carbon suboxide ( $\text{C}_3\text{O}_2$ ) is formed when

- (a) carbon reacts with conc.  $\text{H}_2\text{SO}_4$   
(b) malonic acid reacts with  $\text{P}_4\text{O}_{10}$   
(c) carbon reacts with strong alkali solution  
(d) oxalic acid is heated strongly

5.  $\text{SiCl}_4$  is hydrolysed but  $\text{CCl}_4$  is not hydrolysed because
- Si has vacant  $d$ -orbitals and can accommodate lone-pair of electrons from oxygen of water
  - Si has relatively large size and can increase its coordination number from four to five
  - Si has relatively smaller size and thus interaction with  $\text{H}_2\text{O}$  is spontaneous
  - Si has oxidation number of six while carbon has oxidation number of four in all its compounds.

6. Select correct statement(s).

- In  $\alpha$ -graphite, the layers are arranged in the sequence  $ABAB \dots$
- In  $\beta$ -graphite, the layers are arranged in the sequence  $ABCABC \dots$
- In  $\alpha$ -graphite, the layers are arranged in the sequence  $ABCABC \dots$
- In  $\beta$ -graphite, the layers are arranged in the sequence  $ABAB \dots$

7. Select correct statement(s).

- The enthalpy difference between  $\alpha$ - and  $\beta$ -graphite is very large and thus two forms are not interconvertible
- The enthalpy difference between  $\alpha$ - and  $\beta$ -graphite is very small and two forms are interconvertible
- $\alpha$ -graphite changes to  $\beta$ -graphite at about 1300 K.
- $\beta$ -graphite changes to  $\alpha$ -graphite at about 1300 K

8. Select ionic carbides

- $\text{Al}_4\text{C}_3$ ,  $\text{CaC}_2$ ,  $\text{Mg}_2\text{C}_3$
- $\text{Al}_4\text{C}_3$ ,  $\text{SiC}$ ,  $\text{B}_4\text{C}$
- $\text{CaC}_2$ ,  $\text{Mg}_2\text{C}_3$
- $\text{CaC}_2$ ,  $\text{SiC}$ ,  $\text{Mg}_2\text{C}_3$

9. Silly putty

- is a silicone polymer
- has a composition intermediate between silicone oils and silicone rubbers
- is an asbestos
- is not related to any chemical.

10. The great thermal and chemical stability of silicones is attributed to high strength of

- silicon-carbon bond
- silicon-oxygen bond
- silicon-silicon bond
- carbon-carbon bond

11. Correct statement(s) out of the following is

- $\text{N}(\text{CH}_3)_3$  has pyramidal structure
- $\text{N}(\text{SiH}_3)_3$  shows planar arrangement
- $\text{SiC}$  is highly volatile
- $\text{SiO}_2$  is called silane

12. Group 14 (carbon family) elements have the following properties

- They are all network solids with octahedral network
- Only  $\text{SiO}_2$  is a network solid with tetrahedral coordination and is a giant molecule
- $\text{SnO}_2$  and  $\text{PbO}_2$  are amphoteric oxides.
- All oxides are acidic

13. Silicones

- are synthetic polymer containing repeating ( $\text{R}_2\text{SiO}_2$ ) units
- are formed by hydrolysis of  $\text{R}_2\text{SiCl}_2$
- are natural occurring repeating ( $\text{SiO}_4$ ) units
- single  $\text{R}_2\text{SiO}_2$  unit

14. Select correct statement(s).

- $\text{COCl}_2$  is called phosphine gas
- $\text{C}_3\text{O}_2$  (carbon suboxide) has  $sp^2$  hybridised carbons
- $\text{CO}$  is toxic because it forms a complex with haemoglobin in the blood
- Diamond is unaffected by concentrated acid but graphite is oxidised to mellitic acid with concentrated  $\text{HNO}_3$ .

15. Gases responsible for "green-house effect" are

- $\text{CO}_2$
- $\text{H}_2\text{O}$
- $\text{O}_3$
- $\text{N}_2$

## Passage Comprehension Questions

### Passage 1

Questions are based on following medical report.

In the first biological application of buckyball, chemists at the University of California at San Francisco and Santa Barbara made a discovery in 1993 that could help in designing drugs to treat AIDS. The human immunodeficiency virus (HIV) that causes AIDS reproduces by synthesising a long protein chain, which is cut into smaller segments by an enzyme called HIV-protease. One way to stop AIDS, then, might be to inactivate the enzyme. When the chemists reacted a water-soluble derivative of buckyball with HIV-protease, they found that it binds to the portion of the enzyme that would ordinarily cleave the reproductive protein, thereby preventing the HIV virus from reproducing. Consequently, the virus could no longer infect the human cells they had grown in the laboratory. The buckyball compound itself is not a suitable drug for use against AIDS because of potential side effects and delivery difficulties, but it does provide a model for the development of such drugs.

1. Buckyball is the allotrope of

- phosphorus
- sulphur
- carbon
- titanium

2. What is the formula of the buckyball?

- $\text{P}_4$
- $\text{S}_8$
- $\text{Ti}_3$
- $\text{C}_{60}$

3. In buckyball each atom is

- $sp^2$  hybridized element with extensive delocalised molecular orbital
- $sp^2$  hybridised element with localised molecular orbital
- $sp^3$  hybridised element with delocalised molecular orbital
- $sp^3$  hybridised element with localised molecular orbital

4. Consider following statements about buckyball  
 A : It is also called fullerenes  
 B : It is also called buckminster fullerene  
 C : Bucky tubes (made of fullerenes) are several times stronger than steel wires  
 D : Buckyball is a plastic polymer

Select correct statement(s).

- (a) A, C, D (b) A, B, C  
 (d) A, B, D (d) B, C, D

### Passage 2

Read the following discovery and answer the questions at the end.

"Elemental carbon appears in many structural forms or allotropes. Three of these forms are crystalline—diamond, graphite and the recently discovered fullerenes (buckyball)—while more than 40 others, including coke and carbon black, are amorphous. Now there seems to be set a fourth crystalline allotrope of carbon, reported in 1995 by Richard Lagow at the University of Texas."

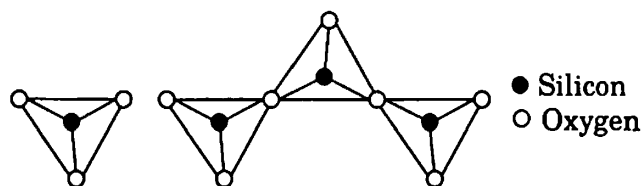
- Newly discovered allotrope of carbon has the form  
 (a) polyene (b) fullerene  
 (c) buckyball (d) none of these
- Structures of different allotropes of carbon have been compared. Which represents incorrect comparison?  
 (a) Allotrope discovered in 1995  $sp$ -hybridised carbon  
 (b) Buckyball  $sp$ -hybridised carbon  
 (c) Graphite  $sp^2$ -hybridised carbon  
 (d) Diamond  $sp^3$ -hybridised carbon

### Passage 3

Read the following short write-up and answer the questions at the end of it.

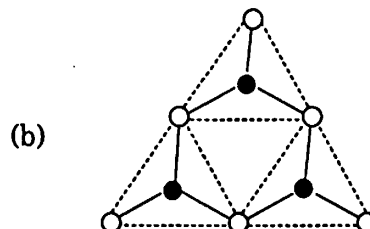
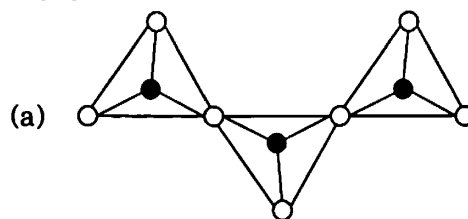
The name 'silica' covers an entire group of minerals, which have the general formula  $\text{SiO}_2$ , the most common of which is **quartz**. Quartz is a framework silicate with  $\text{SiO}_4$  tetrahedra arranged in spirals. *The spirals can turn in a clockwise or anti-clockwise direction—a feature that results in there being two mirror images, optically active, varieties of quartz.*

1. The following pictures represent various silicate anions. Their formulae are respectively:



- (a)  $\text{SiO}_3^{2-}$   $\text{Si}_3\text{O}_7^{2-}$   
 (b)  $\text{SiO}_4^{4-}$   $\text{Si}_3\text{O}_{10}^{8-}$   
 (c)  $\text{SiO}_4^{2-}$   $\text{Si}_3\text{O}_9^{2-}$   
 (d)  $\text{SiO}_3^{4-}$   $\text{Si}_3\text{O}_7^{8-}$

2.  $\text{Si}_3\text{O}_9^{6-}$  (having three tetrahedra) is represented as



- (c) both (a) and (b)  
 (d) none of the above

3. The silicate anion in the mineral kinoite is a chain of three  $\text{SiO}_4$  tetrahedra that share corners with adjacent tetrahedra. The mineral also contains  $\text{Ca}^{2+}$  ions,  $\text{Cu}^{2+}$  ions, and water molecules in a 1 : 1 : 1 ratio mineral is represented as

- (a)  $\text{CaCuSi}_3\text{O}_{10} \cdot \text{H}_2\text{O}$  (b)  $\text{CaCuSi}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$   
 (c)  $\text{Ca}_2\text{Cu}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$  (d) None of these

### Passage 4

Based on following short report, answer the questions given at the end.

In some foam-type fire extinguishers, the reactants are  $\text{Al}_2(\text{SO}_4)_3(\text{aq})$  and  $\text{NaHCO}_3(\text{aq})$ . When the extinguisher is activated, these reactants are allowed to mix producing  $\text{Al}(\text{OH})_3(\text{s})$  and  $\text{CO}_2(\text{g})$ . The  $\text{Al}(\text{OH})_3\text{--CO}_2$  foam extinguishes the fire.

- $\text{CO}_2$  is formed as a result of  
 (a) reaction between  $\text{Al}^{3+}$  and  $\text{HCO}_3^-$   
 (b) reaction between hydrolysis product of  $\text{Al}^{3+}$  and  $\text{HCO}_3^-$   
 (c) reaction between hydrolysis product of  $\text{NaHCO}_3$  and  $\text{Al}_2(\text{SO}_4)_3$   
 (d) direct reaction between  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{NaHCO}_3$
- Net ionic reaction of the above chemical change is  
 (a)  $\text{Al}^{3+} + \text{HCO}_3^- + \text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_3 + \text{CO}_2$   
 (b)  $\text{Al}^{3+} + \text{HCO}_3^- + \text{OH}^- \longrightarrow \text{Al}(\text{OH})_3 + \text{CO}_2 + \text{H}_2\text{O}$   
 (c)  $[\text{Al}(\text{H}_2\text{O})_6]^{3+} + \text{HCO}_3^- \longrightarrow \text{Al}(\text{OH})_3 + \text{CO}_2 + \text{H}_2\text{O}$   
 (d)  $\text{Al}_2(\text{SO}_4)_3 + \text{NaHCO}_3 \longrightarrow \text{Na}_2\text{SO}_4 + \text{Al}(\text{OH})_3 + \text{H}_2\text{O}$

3. Addition of  $\text{Na}_2\text{CO}_3$  to a solution of an oxide in water produces  $\text{CO}_2$ . This experiment indicates that
- the oxide is that of a non-metal
  - the oxide is basic
  - the oxide is amphoteric
  - the oxide is neutral

### Passage 5

Questions given below are based on following technical report.

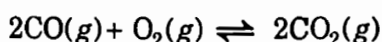
The  $\text{CO}_2$  as well as  $\text{H}_2\text{O}$  absorbs strongly in the infrared region, and its presence in the atmosphere decreases the loss of heat from the earth by radiation. This global warming is called the 'green house effect' (other gases, including the oxides of nitrogen from car exhausts, freons from aerosols and refrigerators and methane from bacteria in the soil and in the rumen of cows, also add to the green house effect). The concentration of atmospheric  $\text{CO}_2$  has increased by 10%. This is resulting in the increase in the mean temperature of the earth by  $2.5^\circ\text{C}$ , varying from  $2^\circ\text{C}$  at the equator to  $4^\circ\text{C}$  at the poles. This could have dramatic effects on the climate.

- As a result of green house effect, there can be
  - increase in rate of evaporation of water, thus, untimely more rain, flooding, etc.
  - tropical storms in certain parts of the world
  - decrease in pH of the soil
  - increase in pH of the soil
 Select correct alternate  
 (a) B, C, D                      (b) A, C, D  
 (c) A, B, D                      (d) A, B, C
- Which of the following is growing at a faster rate than  $\text{CO}_2$  thus responsible for the green house effect?
  - CFC
  - $\text{N}_2\text{O}$
  - $\text{O}_3$
  - $\text{CH}_4$

3. Instead of monitoring carbon dioxide, suggest another gas that scientists could study to substantiate the fact that  $\text{CO}_2$  concentration is steadily increasing in the atmosphere

- $\text{N}_2\text{O}$
- $\text{O}_2$
- $\text{CH}_4$
- $\text{O}_3$

4. The equilibrium constant ( $K_p$ ) for the reaction



is  $1.4 \times 10^{90}$  at  $25^\circ\text{C}$ . Given this enormous value, why doesn't CO convert totally to  $\text{CO}_2$  in the troposphere?

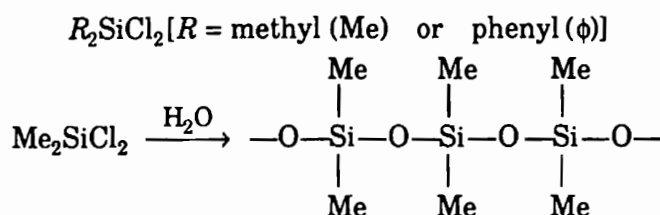
- CO forms complex with haemoglobin
- CO has low solubility in  $\text{H}_2\text{O}$
- CO has high activation energy
- CO is toxic in nature

### Passage 6

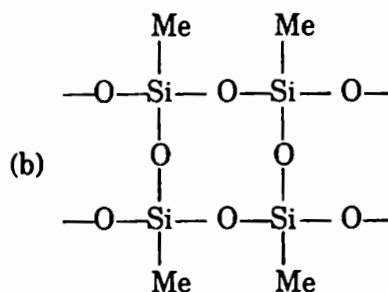
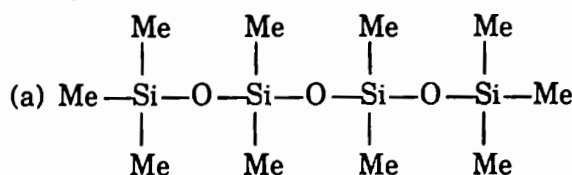
Read the following write-ups and answer the questions at the end of it.

Silicones are synthetic polymers containing repeated  $\text{R}_2\text{SiO}$  units. Since, the empirical formula is that of a ketone ( $\text{R}_2\text{CO}$ ), the name silicone has been given to these materials. Silicones can be made into oils, rubbery elastomers and resins. They find a variety of applications because of their chemical inertness, water repelling nature, heat-resistance and good electrical insulating property.

Commercial silicon polymers are usually methyl derivatives and to a lesser extent phenyl derivatives and are synthesised by the hydrolysis of

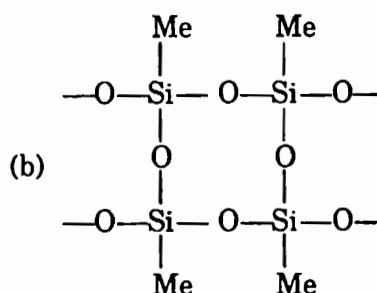
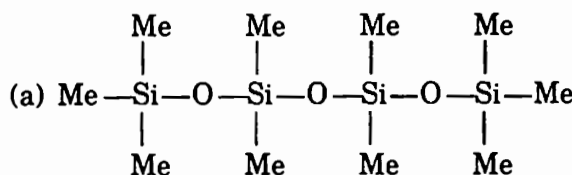


1. If we mix  $\text{SiMe}_3\text{Cl}$  with  $\text{SiMe}_2\text{Cl}_2$ , we get silicones of the type



- both (a) and (b)
- None of the above

2. If we start with  $\text{SiMeCl}_3$  as the starting material, silicones formed is



- both (a) and (b)
- None of the above

## Assertion & Reason

**Codes :**

- Both **A** and **R** are true and **R** is the correct explanation of **A**.
- Both **A** and **R** are true but **R** is not the correct explanation of **A**.
- A** is true but **R** is false.
- A** is false but **R** is true.

- Assertion (A) :**  $\text{SiF}_6^{2-}$  is known but  $\text{SiCl}_6^{2-}$  is not known.

**Reason (R) :** Interaction of F lone pair electrons with Si is stronger than that of chlorine and due to smaller size of F steric repulsion will be less.

- Assertion (A) :** If a metal exhibits more than one oxidation state, the halide in the higher oxidation state will be more covalent than the one in lower oxidation state.

**Reason (R) :**  $\text{SnCl}_4$ ,  $\text{PbCl}_4$ ,  $\text{SbCl}_5$  and  $\text{UF}_6$  are more covalent than  $\text{SnCl}_2$ ,  $\text{PbCl}_2$ ,  $\text{SbCl}_3$  and  $\text{UF}_4$ .

- Assertion (A) :** CO is toxic.

**Reason (R) :** CO forms complex with haemoglobin in the blood, and this complex is more stable than oxy-haemoglobin.

- Assertion (A) :** Lime water turns milky when the gas liberated from an acidified carbonate solution is passed into it.

**Reason (R) :** The liberated  $\text{CO}_2$  reacts with lime water to give calcium bicarbonate as the precipitate.

- Assertion (A) :**  $\text{PbCl}_2$  is more stable than  $\text{PbCl}_4$ .

**Reason (R) :**  $\text{PbCl}_4$  is powerful oxidising agent.

- Assertion (A) :**  $\text{SiCl}_4$  is easily hydrolysed as compared to  $\text{CCl}_4$ .

**Reason (R) :** Silicon can extend its coordination number beyond four.

- Assertion (A) :**  $\text{N}(\text{CH}_3)_3$  is pyramidal but  $\text{N}(\text{SiH}_3)_3$  is planar.

**Reason (R) :** In  $\text{N}(\text{SiH}_3)_3$  lone-pair on N-atom is transferred to the empty *d*-orbitals of silicon ( $p\pi-d\pi$  overlapping).

- Assertion (A) :** Between  $\text{SiCl}_4$  and  $\text{CCl}_4$ , only  $\text{SiCl}_4$  reacts with water.

**Reason (R) :**  $\text{SiCl}_4$  is ionic and  $\text{CCl}_4$  is covalent.

- Assertion (A) :** Large number of organic compounds are formed with long carbon-chain.

**Reason (R) :** Maximum catenation occurs in carbon atoms.

- Assertion (A) :** Graphite cannot be converted into diamond.

**Reason (R) :** Graphite is conducting in nature.

- Assertion (A) :** Diamond is insulator and graphite is conducting.

**Reason (R) :** C-atom is  $sp^3$  hybridised in both.

- Assertion (A) :** Carbon dioxide is a gas but silicon dioxide is an infusible solid.

**Reason (R) :** Carbon dioxide has a linear  $\pi$ -bonded structure.

## True & False

- $\text{N}(\text{CH}_3)_3$  and  $\text{N}(\text{SiH}_3)_3$  both have  $sp^3$ -hybridised N-atom and pyramidal structure.
- $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  both form soluble complex with  $\text{CN}^-$  but are decomposed by  $\text{H}_2\text{S}$ .
- Quartz is framework silicate with  $\text{SiO}_4$  tetrahedra arranged in spirals.
- Silicones are synthetic polymers containing repeated  $\text{R}_2\text{SiO}$  units.
- $\text{Fe}_2\text{O}_3$  and  $\text{CuO}$  impart green colour to the glass.
- $\text{PbO}_2$  is called red-lead.
- $\text{Pb}_3\text{O}_4$  on reaction with  $\text{HNO}_3$  forms  $\text{Pb}(\text{NO}_3)_2$  and  $\text{PbO}_2$ .
- Ultra pure silicon is prepared by reduction of  $\text{SiO}_2$  with carbon.
- Si becomes a *p*-type semiconductor when doped with group 13 element (Al, Ga).
- Si becomes an *n*-type semiconductor when doped with group 15 element (P, As).
- Graphite is the least stable form of carbon.
- $\text{Pb}(\text{II})$  salts are easily oxidised to  $\text{Pb}(\text{IV})$  salts.
- $\text{SnCl}_2$  is better reducing agent than  $\text{HgCl}_2$ .
- Finely divided lead powder is pyrophoric.
- Pb does not dissolve in hot concentrated  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ .

## Fill in the Blanks

- Silicon is the ..... abundant element by mass in the earth's crust.
- Graphite consists of planar hexagonal layers of carbon atoms held together by .....
- Silicon exists only in the ..... structure due to tendency to form  $p\pi-p\pi$  bonds to itself.
- In case of  $\text{N}(\text{CH}_3)_3$ , geometry is ..... and in case of  $\text{N}(\text{SiH}_3)_3$  geometry is .....
- Dry ice is .....
- $\text{Be}_2\text{C}$  and  $\text{Al}_4\text{C}_3$  are called ..... because they react with  $\text{H}_2\text{O}$  yielding methane.
- The cyanide ions are toxic because they bind almost irreversibly to the  $\text{Fe}(\text{III})$  ion in .....

8. The  $\text{CO}_2$  as well as  $\text{H}_2\text{O}$  absorbs strongly in the infrared region and its presence in the atmosphere decreases the loss of heat from the earth by radiation. This global warming is called .....
9.  $\text{Si}_3\text{N}_4$ ,  $\text{B}_4\text{C}$  and  $\text{SiC}$  are ..... ceramics.
10.  $\text{SiO}_2$  is .....,  $\text{GeO}_2$  is .....  $\text{SnO}$  is ..... and  $\text{PbO}$  is .....
11. Concentrated  $\text{HNO}_3$  converts graphite into .....
12.  $\text{CCl}_4$  is kinetically stable towards .....
13.  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  changes to ..... on heating at  $80^\circ\text{C}$ .
14.  $\text{C}_{60}\text{K}$  is an .....
15. Graphite fluoride and graphite oxide are .....

### Matrix-Match Type Questions

#### I. One Or More Correct

1. Match the oxide of Column I with their corresponding property (ies) in Column II.

| Column I                   | Column II             |
|----------------------------|-----------------------|
| A. $\text{Pb}_3\text{O}_4$ | 1. oxidation state +2 |
| B. $\text{SnO}_2$          | 2. oxidation state +4 |
| C. $\text{PbO}_2$          | 3. amphoteric         |
| D. $\text{CO}_2$           | 4. basic              |
| E. $\text{GeO}$            | 5. acidic             |

2. Match the species in Column I with their corresponding property (ies) in Column II.

| Column I                        | Column II              |
|---------------------------------|------------------------|
| A. $\text{CO}_2$                | 1. Dry ice             |
| B. $\text{Al}_2(\text{SO}_4)_3$ | 2. Fire extinguisher   |
| C. $\text{KCN}$                 | 3. Acidic              |
| D. $\text{CaC}_2$               | 4. Ligand              |
| E. $\text{Mg}_2\text{C}_3$      | 5. $sp$ -hybridisation |
|                                 | 6. Green house effect  |

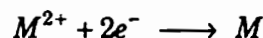
### Integer Answer Types

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the ORS have to be darkened. For example, if the correct answers to question number X, Y, Z and W (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will like the following :

|   | X | Y | Z | W |
|---|---|---|---|---|
| ① | ① | ① | ① | ① |
| ② | ② | ② | ② | ② |
| ③ | ③ | ③ | ③ | ③ |
| ④ | ④ | ④ | ④ | ④ |
| ⑤ | ⑤ | ⑤ | ⑤ | ⑤ |
| ⑥ | ⑥ | ⑥ | ⑥ | ⑥ |
| ⑦ | ⑦ | ⑦ | ⑦ | ⑦ |
| ⑧ | ⑧ | ⑧ | ⑧ | ⑧ |
| ⑨ | ⑨ | ⑨ | ⑨ | ⑨ |

#### Set I

1. Total number of atoms of carbon and oxygen in graphite oxide .....
2. When malonic acid is dehydrated using  $\text{P}_4\text{O}_{10}$  at  $150^\circ\text{C}$ , species formed has total number of atoms .....
3. Number of isotopes of carbon .....
4. How many of the following oxides are basic oxides?  
 $\text{CO}_2$ ,  $\text{SnO}_2$ ,  $\text{PbO}$ ,  $\text{PbO}_2$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{Al}_2\text{O}_3$
5. For the half-cell reaction,



$E^\circ$  (in volts) are given for different metals

| Cu   | Zn    | Fe    | Pb    | Sn    |
|------|-------|-------|-------|-------|
| 0.34 | -0.76 | -0.48 | -0.13 | -0.14 |

How many of these metals can reduce  $\text{Cu}^{2+}$  to  $\text{Cu}$ ?

6. Out of the elements C, S, Ge, Sn and Pb only +4 oxidation state is shown by how many element(s)?
7. More than four bonds are made with how many elements in carbon family?
8. How many elements in group 14 are used as semiconductor?

#### Set II

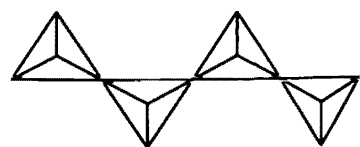
1. How many of the following have two  $\sigma$  and two  $\pi$  bonds?  
 $\text{C}_3^{4-}$ ,  $\text{CN}_2^{2-}$ ,  $\text{CO}_2$ ,  $\text{C}_2^{2-}$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CN}^-$
2. How many of the fuel gases have CO and  $\text{H}_2$  both as combustible gases?  
LPG, water gas, Producer gas, Coal gas, CNG
3. A silicate mineral has three  $\text{SiO}_4$  tetrahedra that share corners with adjacent tetrahedra. Mineral also contains  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{H}_2\text{O}$  in 1:1:1 molar ratio. Thus, total number of atoms of Cu, Si and Ca per unit of mineral is .....
4. A mixture contains 3 moles of CO and  $\text{CO}_2$ . On passing the mixture over heated charcoal, volume increases to 5 moles. Thus,  $\text{CO}_2$  in the mixture is ..... mole(s).
5. Total number of  $\sigma$  and  $\pi$  bonds in carbon suboxide ( $\text{C}_3\text{O}_2$ ) is .....
6. What is total negative charge on the silicate  $[\text{Si}_4\text{O}_{11}]$ ?
7.  $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$ ,  $K = 10^{-9}$  at 300 K. What is  $p_{\text{CO}_2}$ ?
8. Inert pair effect is shown by how many elements? Ga, Al, Tl, Pb, Sn, Ge

# Answers & Solutions

## Master Exercises

### Exercise 1

#### Short Answer Type Questions

- Due to available  $d$ -orbital in which  $(n-1)p$  electrons, can be excited to make C.N. of six. Carbon lacks  $d$ -orbital.
- (a) Pb (b) C (c) Si (d) C
- (a)  $\text{CCl}_4$ ,  $\text{CO}_2$  (b) CO (c)  $\text{CH}_4$
- Diamond is very hard, high melting solid. It is an electrical insulator. Diamond has a covalent network structure in which each C-atom uses  $sp^3$ -hybrid orbitals to form a tetrahedral array of  $\sigma$ -bonds. The interlocking, three-dimensional network of strong bonds makes diamond the hardest known substance with highest m.p. for an element. Because the valence electrons are localised in the  $\sigma$ -bonds, diamond is an electrical insulator.
- (a) (A) A :  $\text{SiF}_4$   
(B) :  $\text{H}_2\text{SiF}_6$  ]  
(C) :  $\text{H}_4\text{SiO}_4$  ]  
 $3\text{SiF}_4 + 4\text{H}_2\text{O} \longrightarrow \text{H}_4\text{SiO}_4 + 2\text{H}_2\text{SiF}_6$   
(b) (D) :  $\text{C}_6(\text{COOH})_6$ , mellitic acid (benzene hexacarboxylic acid)  
(c) (E) :  $(\text{Na}_2\text{SiO}_3 + \text{C})$
- $\text{CO}_3^{2-} + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + 2\text{OH}^-$   
 $\text{CO}_3^{2-}$  solution is alkaline due to hydrolysis.
- The  $\text{Ca}^{2+}$  ions give precipitates (scum) with soaps. On heating the  $\text{HCO}_3^-$  ions revert to  $\text{CO}_3^{2-}$  which gives a precipitate with  $\text{Ca}^{2+}$  ions :  
 $\text{Ca}(\text{HCO}_3)_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$
- Al reacts with NaOH forming  $\text{H}_2$  gas. NaOH is formed due to hydrolysis of  $\text{Na}_2\text{CO}_3$  (Q. 6 above)  
 $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaAlO}_2 + 3\text{H}_2$
- $2\text{NO}(g) + \text{CS}_2 \longrightarrow \underset{\text{yellow solid}}{2\text{S}(s)} + \text{N}_2(g) + \text{CO}_2(g)$
- $\text{Na}_2\text{CO}_3$  formed when atmospheric  $\text{CO}_2$  reacts with NaOH.
- (a) To provide a "bite" in soft drinks.  
 $\text{CO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq)$   
(b) As fire extinguisher;  $\text{CO}_2$  is non-flammable and 1.5 times more dense than air.  
(c) As refrigerant; dry ice sublimates at  $-78^\circ\text{C}$ .
- No, as such a high charge separation is unlikely.
- $\ominus : \text{C} :: \text{C} : \ominus \quad \ominus : \overset{\ominus}{\underset{\ominus}{\text{C}}} :: \text{C} :: \text{C} : \ominus$
- Refer text.
- $\text{Be}_2\text{C}$  and  $\text{Al}_4\text{C}_3$  are ionic carbides; oxidation state of carbon = -4
- $\text{H}_2\text{O}$     17.  $\text{O}_2$
- Due to high activation energy.
- Highly lustrous form (in layer) of carbon is called glanzkohlenstoff. It consists of very small crystals of graphite. It is found to have greater adsorption power and greater hardness than graphite. This crystalline form is obtained when the flame of burning methane is impinged on glazed porcelain placed at 900 K.
- van der Waals' forces
- $\text{SiO}_2(s) + \text{Na}_2\text{SO}_4(s) \longrightarrow \text{Na}_2\text{SiO}_3(s) + \text{SO}_3(g)$
- $\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{Si}}}-\text{O}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{Si}}}-\text{CH}_3$
- $(\text{CH}_3\text{COO})_3\text{SiCH}_3$ . This would give the cross-linking for necessary strength.
- (a)  $\text{SiO}_4^{4-}$  (b)  $\text{Si}_3\text{O}_{10}^{8-}$  (c)  $\text{Si}_4\text{O}_{12}^{8-}$
- (a)   $\text{SiO}_4^{4-}$   
(b)   $\text{Si}_4\text{O}_{13}^{10-}$
- (X) :  $\text{HgCl}_2$   
(Y) :  $\text{HgS}$   
(Z) :  $\text{Hg}_2\text{Cl}_2$
- Sn is treated with HCl gas to make anhydrous  $\text{SnCl}_4$ .
- HF attacks silicates of glass  
 $\begin{cases} \text{CaSiO}_3 + 6\text{HF} \longrightarrow \text{CaSiF}_6 + 3\text{H}_2\text{O} \\ \text{Na}_2\text{SiO}_3 + 6\text{HF} \longrightarrow \text{Na}_2\text{SiF}_6 + 3\text{H}_2\text{O} \end{cases}$
- (a) supercooled (b) HF (c) PbO (d)  $\text{B}_2\text{O}_3$   
(e)  $\text{CaF}_2$

## Analytical Questions

- (i) There is feasibility of  $p$ - $p$   $\pi$  bond in silicon.  
(ii)  $\pi$ -bonding between oxygen and silicon involving  $p$ - and  $d$ -orbitals decreases availability of lone-pairs of electrons on oxygen.

### 2. (a) Triple points : Two Phase

Point A : Graphite  $\rightleftharpoons$  Liquid  $\rightleftharpoons$  Vapour

Point B : Diamond  $\rightleftharpoons$  Graphite  $\rightleftharpoons$  Liquid

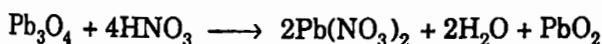
(b) Diamond

(c) Apply high pressure at high temperature

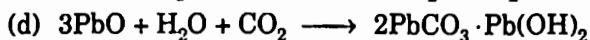
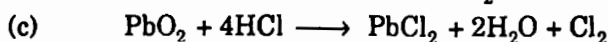
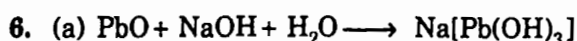
### 3. (a) Sn (b) Cl (c) Sn (d) Se (e) B

- Carbon forms various stable compounds with itself and other elements such as N, O, H, S. Bimolecules contain chains and rings with many C—C bonds. Si—Si bonds are much less stable and chain of Si atoms are uncommon.

- $\text{Pb}_3\text{O}_4$  on reaction with  $\text{HNO}_3$  forms  $\text{Pb}(\text{NO}_3)_2$  and  $\text{PbO}_2$ .



2 moles of  $\text{Pb}(\text{NO}_3)_2$  are from dilead(II) oxide while  $\text{PbO}_2$  is from lead(IV) oxide. Thus it is  $2\text{PbO} \cdot \text{PbO}_2$ .



$$7. \text{Moles of } \text{CO}_2 \text{ formed} = n = \frac{pV}{RT}$$

$$= \frac{775}{760} \times \text{atm} \times 100 \text{ L}$$

$$= 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 303 \text{ K}$$

$$= 4.0992$$

If 2 moles  $\text{CO}_2$  are formed then

$\text{MgSiO}_3$  precipitated is = 1 mol

and when 4.0992 moles  $\text{CO}_2$

$$\text{and formed } \text{MgSiO}_3 \text{ would be} = \frac{4.0992}{2}$$

$$= 2.0496 \text{ mol}$$

(molar mass of  $\text{MgSiO}_3 = 100 \text{ g mol}^{-1}$ )

$$= 2.0496 \times 100 \text{ g}$$

$$= 204.96 \text{ g}$$

8. Refer text.

## NCERT Problems

Refer Text

## Exercise 2

### Only One Option Correct

- |          |          |          |          |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 1. (a)   | 2. (b)   | 3. (c)   | 4. (d)   | 5. (c)   | 6. (d)   | 7. (c)   | 8. (a)   | 9. (a)   | 10. (d)  |
| 11. (b)  | 12. (c)  | 13. (a)  | 14. (a)  | 15. (b)  | 16. (c)  | 17. (b)  | 18. (d)  | 19. (d)  | 20. (b)  |
| 21. (d)  | 22. (c)  | 23. (c)  | 24. (a)  | 25. (b)  | 26. (a)  | 27. (c)  | 28. (d)  | 29. (d)  | 30. (d)  |
| 31. (d)  | 32. (d)  | 33. (b)  | 34. (d)  | 35. (d)  | 36. (a)  | 37. (b)  | 38. (b)  | 39. (b)  | 40. (a)  |
| 41. (a)  | 42. (a)  | 43. (c)  | 44. (b)  | 45. (c)  | 46. (d)  | 47. (c)  | 48. (b)  | 49. (b)  | 50. (d)  |
| 51. (a)  | 52. (b)  | 53. (d)  | 54. (b)  | 55. (d)  | 56. (b)  | 57. (d)  | 58. (d)  | 59. (a)  | 60. (a)  |
| 61. (c)  | 62. (d)  | 63. (d)  | 64. (c)  | 65. (a)  | 66. (d)  | 67. (d)  | 68. (a)  | 69. (a)  | 70. (a)  |
| 71. (c)  | 72. (d)  | 73. (a)  | 74. (d)  | 75. (b)  | 76. (b)  | 77. (c)  | 78. (b)  | 79. (d)  | 80. (b)  |
| 81. (b)  | 82. (c)  | 83. (b)  | 84. (d)  | 85. (a)  | 86. (d)  | 87. (d)  | 88. (a)  | 89. (b)  | 90. (b)  |
| 91. (d)  | 92. (d)  | 93. (a)  | 94. (c)  | 95. (b)  | 96. (a)  | 97. (d)  | 98. (a)  | 99. (b)  | 100. (c) |
| 101. (c) | 102. (d) | 103. (b) | 104. (d) | 105. (c) | 106. (c) | 107. (d) | 108. (a) | 109. (a) | 110. (b) |
| 111. (a) | 112. (c) | 113. (b) | 114. (a) | 115. (c) |          |          |          |          |          |

### One or More Than One Options Correct

- (a,b,c,d)
- (a,b,c,d)
- (a,b,c,d)
- (b)
- (a,b)
- (a,b)
- (b,d)
- (a)
- (a,b)
- (a,b)
- (a,b)
- (b,c)
- (a,b)
- (c,d)
- (a,b)

## Passage Comprehension Questions

### Passage 1

- (c)
- (d)
- (a)
- (b)

### Passage 2

- (a)
- (b)



|             |   |   |   |   |   |   |   |   |
|-------------|---|---|---|---|---|---|---|---|
| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Answers →   | 3 | 2 | 7 | 2 | 8 | 6 | 9 | 5 |
|             | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
|             | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|             | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
|             | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
|             | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
|             | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
|             | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
|             | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
|             | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
|             | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |

"Whether it may be laughing gas (which does not make you laugh) or Holme's signal or flickering light (called 'will-o-the-wisp') are clues from Nitrogen family"

# 13

## Group 15 (VA—The Nitrogen Family)

The elements in this group (N, P, As, Sb, Bi) are also called Pnictogen (pnictogen) or pnictides from the Greek synonym for choking (as nitrogen does not support combustion). The elements N and P are essential constituents of the living system. Heavier members of the group, particularly arsenic are extremely toxic.

Nitrogen is highly abundant (about 78% by volume and 75% by mass) in air as  $N_2$ . However abundance of nitrogen in rocks and soils is low (19 ppm) as  $KNO_3$  and  $NaNO_3$ .

Naturally occurring nitrogen consists of  $^{14}N$  stable isotope,  $^{15}N$  also occurs slightly, relative abundance being  $^{14}N/^{15}N$  ~272 : 1

Phosphorus is highly abundant in crystal rocks ( $\approx 1120$  ppm) most as orthophosphate. It also occurs in plants and animals where it is an essential constituent of life.

$^{31}P$  is the only stable isotope of phosphorus. Among six radioactive isotopes,  $^{32}P$  ( $\beta$ -emitter) is most important.

The elements As, Sb, Bi have very low abundances

As < 2 ppm

Sb 0-2 ppm

Bi 0-01 ppm

They occur as sulphides ( $As_2S_3$ ,  $Sb_2S_3$ ,  $Bi_2S_3$ ) and are thus chalcophilic.

### Learning Framework of the Chapter

- Group 15 —Periodicity Study of Nitrogen and its Compounds
- Study of Phosphorus and its Compounds

|             |
|-------------|
| ${}^7N$     |
| ${}^{15}P$  |
| ${}^{33}As$ |
| ${}^{51}Sb$ |
| ${}^{83}Bi$ |

## Group 15 — Periodicity

Physical properties of the elements in nitrogen family [Group 15 (VA)] are summarised in Table 13.1 and Fig. 13.1.

Table 13.1 Physical Properties of the Elements of Group 15 (VA)

|                                                      | N                                   | P                        | As                       | Sb                       | Bi                               |
|------------------------------------------------------|-------------------------------------|--------------------------|--------------------------|--------------------------|----------------------------------|
| Electronic configuration                             | [He] $2s^2 2p^3$                    | [Ne] $3s^2 3p^3$         | [Ar] $3d^{10} 4s^2 4p^3$ | [Kr] $4d^{10} 5s^2 5p^3$ | [Xe] $4f^{14} 5d^{10} 6s^2 6p^3$ |
| Electronegativity (Pauling) $IE \text{ kJ mol}^{-1}$ | 3.0                                 | 2.1                      | 2.0                      | 1.9                      | 1.9                              |
| $(IE)_1$                                             | 1403                                | 1012                     | 947                      | 834                      | 703                              |
| $(IE)_2$                                             | 2857                                | 1897                     | 1950                     | 1590                     | 1610                             |
| $(IE)_3$                                             | 4578                                | 2910                     | 2732                     | 2440                     | 2467                             |
| Melting point/ $^{\circ}\text{C}$                    | -210                                | 44 (white)<br>597 (red)  | 816                      | 631                      | 271                              |
| Boiling point/ $^{\circ}\text{C}$                    | -195.8                              | 281 (white)<br>431 (red) | 615<br>(sublimes)        | 1587                     | 1564                             |
| Atomic radius/ pm                                    | 74                                  | 110                      | 121                      | 141                      | 152                              |
| Principal oxidation number                           | +3, 0, +5, -3, -2, -1 +1,<br>+2, +4 | +3, +5                   | +3, +5                   | +3, +5                   | +3                               |
| Abundance                                            |                                     |                          | 0.0002%                  | 0.00002%                 | 0.00002%                         |
| Physical state (1 atm, $25^{\circ}\text{C}$ )        | gas                                 | solid                    | solid                    | solid                    | solid                            |

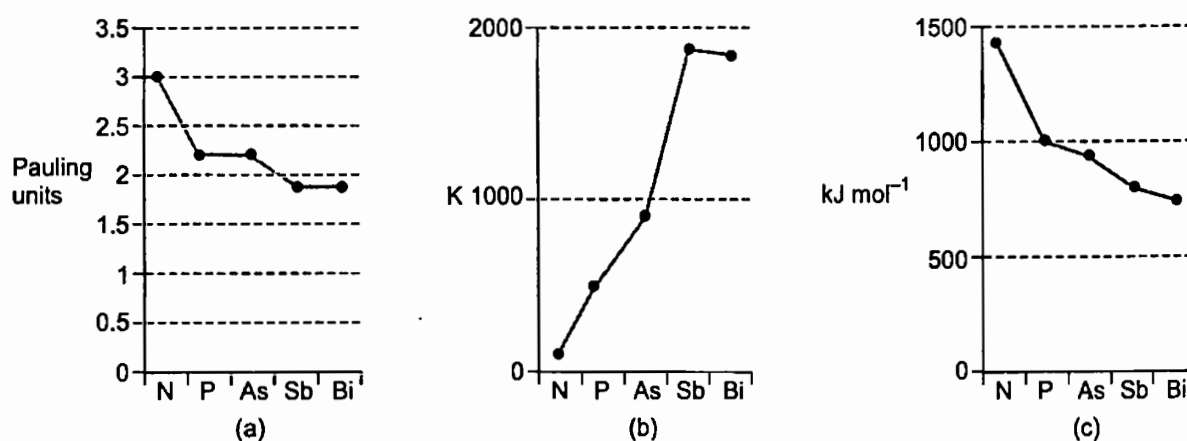


Fig. 13.1 Some group trends of the group 15 elements: (a) Pauling electronegativity, (b) Boiling point, and the (c) First ionisation energy

### Physical State

Group 15 elements are sometimes referred to as **pnictogens**. All the elements are important and bismuth is notable for being the heaviest element with non-radioactive isotope.

Elements of this group show a systematic gradation of properties (Table 13.1) Nitrogen is gaseous in nature and exists as a diatomic molecule  $\text{N}=\text{N}$ . This is due to the very high bond energy of the  $\text{N}=\text{N}$  bond,  $946 \text{ kJ mol}^{-1}$ , which is nearly six times the  $\text{N}-\text{N}$  bond energy,  $160 \text{ kJ mol}^{-1}$ . On the contrary  $\text{P}=\text{P}$  bond is quite weak, its energy of  $490 \text{ kJ mol}^{-1}$  is only  $\sim 2.5$  times the  $\text{P}-\text{P}$  bond energy,  $209 \text{ kJ mol}^{-1}$ . Therefore, phosphorus exists as tetra-atomic  $\text{P}_4$  molecules in the gaseous state. In the solid state, it exists in different allotropic forms.

The change from non-metallic to metallic character with increase in the atomic number is well illustrated in this group. The first two elements, nitrogen and phosphorus, are non-metals, arsenic and antimony are metalloids whereas bismuth is predominantly metallic in

nature. In keeping with this trend, the electronegativity of these elements decreases gradually on moving down the group. The density, melting and boiling points of the elements increase with increase in atomic number.

### DEEP Focus

#### Radii, IE, Oxidation State

Atomic radii, as expected, increase with increase in atomic number. As a consequence, ionisation energies decrease on descending the group. Nitrogen shows an exceptionally high ionisation energy which is due to its small atomic size. As discussed above, all the elements of this group have five electrons in their valence shell, they exhibit a highest oxidation state of +5 by using all five electrons in forming bonds. As one goes down the group, the tendency of the pair of  $s$  electrons to remain inert increases and only  $p$ -electrons are used in bonding, resulting in an oxidation state of +3. The stability of +3 state relative to the +5 state thus increases on moving down the group. In the case of nitrogen, a very wide range of oxidation state exists :

| Compound                      | Oxidation state of N |
|-------------------------------|----------------------|
| NH <sub>3</sub>               | -3                   |
| N <sub>2</sub> H <sub>4</sub> | -2                   |
| NH <sub>4</sub> OH            | -1                   |
| N <sub>2</sub>                | 0                    |
| N <sub>2</sub> O              | +1                   |
| NO                            | +2                   |
| NO <sub>2</sub>               | +4                   |
| HNO <sub>3</sub>              | +5                   |

The negative oxidation state of nitrogen arise because of its higher electronegativity (3.05) than that of hydrogen (2.1). As you can see from the Table 13.1 the energy required to produce  $M^{5+}$  is so immense that it is never formed. The compounds formed by these elements in +5 oxidation state are thus predominantly covalent. However, in case of Sb and Bi, the sum of the first three ionisation energies is just low enough to form  $M^{3+}$  ions. But fluorine is the only element which gives an electronegativity difference enough to permit the formation of ionic bonds. Thus, SbF<sub>3</sub> and BiF<sub>3</sub> exist as ionic solids.

### DEEP Focus

Since, it is not easy from energy considerations to gain three electrons to achieve stable noble gas configuration, the formation of the tri-negative ion ( $M^{3-}$ ) is rare. But, nitrogen being the smallest and the most electronegative of all the members of the group, forms trivalent anion with reactive metals which have low ionisation energies. Thus, nitrogen forms ionic nitrides such as Li<sub>3</sub>N, Be<sub>3</sub>N<sub>2</sub>, Mg<sub>3</sub>N<sub>2</sub>, Ca<sub>3</sub>N<sub>2</sub>. As the electronegativity of the other elements of the group, i.e., P, As, Sb and Bi, is low, most of their compounds are covalent in nature.

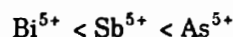
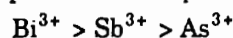
Nitrogen is not able to extend its coordination number beyond four, the other elements have coordination numbers of five as well as six. The extension of coordination number is due to the availability of *d*-orbitals in P, As, Sb and Bi, using which these elements can attain  $sp^3d$  and  $sp^3d^2$  hybridisation, e.g., in PCl<sub>5</sub> and PCl<sub>6</sub><sup>-</sup>, respectively. Thus, **nitrogen does not function as a Lewis acid whereas phosphorus, arsenic, antimony and bismuth do so. The hydrides of this group and their alkyl derivatives act as Lewis bases, forming a number of addition complexes, e.g., (NH<sub>3</sub>·BF<sub>3</sub>), [CaCl<sub>2</sub>·4NH<sub>3</sub>], etc.**

- N and P show the typical properties of non-metals :
  - are poor conductors of heat and electricity,
  - form acidic oxides,
  - form covalent compounds predominantly.

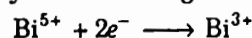
- Metallic nature increases as we go down the group, N and P are typical non-metals, As and Sb are metalloids and Bi is a metal.
- Phosphorus and the other members of the group can make use of *d*-orbitals in their bonding, thus compounds MX<sub>3</sub> as well as MX<sub>5</sub> are formed (PCl<sub>3</sub>, PCl<sub>5</sub> etc.), but NCl<sub>5</sub> is not formed; N does not have *d*-orbital.

### DEEP Focus

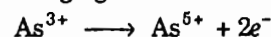
- Stability of +3 state increases and that of +5 state decreases going down the group due to "inert pair effect", thus



Bi<sup>5+</sup> salts are very rare and are good oxidising agents :



As<sup>3+</sup> salts are good reducing agents :



### Nature of Compounds

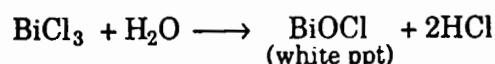
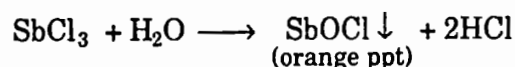
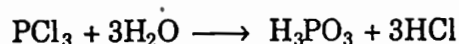
- As we go down the group, basic nature of oxides increases and acidic nature decreases. Oxides of N and P are acidic, those of As and Sb are amphoteric and that of Bi are basic.

| Element | Oxides                                                                                                                                | Trend      |
|---------|---------------------------------------------------------------------------------------------------------------------------------------|------------|
| N       | N <sub>2</sub> O, NO, N <sub>2</sub> O <sub>3</sub> , N <sub>2</sub> O <sub>4</sub> , NO <sub>2</sub> , N <sub>2</sub> O <sub>5</sub> | acidic     |
| P       | P <sub>4</sub> O <sub>6</sub> , P <sub>4</sub> O <sub>10</sub>                                                                        |            |
| As      | As <sub>4</sub> O <sub>6</sub> , As <sub>4</sub> O <sub>10</sub>                                                                      | amphoteric |
| Sb      | Sb <sub>4</sub> O <sub>6</sub> , Sb <sub>4</sub> O <sub>10</sub>                                                                      |            |
| Bi      | Bi <sub>2</sub> O <sub>3</sub>                                                                                                        | basic      |

### DEEP Focus

- They form trihalide and pentahalide (except N, which does not form NCl<sub>5</sub> etc). As we go down the group, covalent nature decreases and ionic nature increases; thus NCl<sub>3</sub> and PCl<sub>3</sub> are covalent while BiCl<sub>3</sub> is ionic. This is also in accordance with **Fajan's rule** : *Smaller the size of cation, larger the size of anion, greater the charge then greater the polarising power and hence greater the covalent nature.*

Halides are hydrolysed in water forming oxyacids or oxychlorides :



- Trihalides (PF<sub>3</sub>) have a pyramidal structure in the gaseous state.
- Nitrogen is relatively unreactive, which is why it has accumulated in such large amounts in the atmosphere.

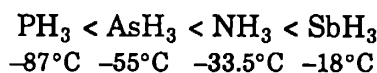
White phosphorus catches fire when exposed to air, burning to form  $P_4O_{10}$ . It is **stored under water to prevent this**. Red phosphorus is stable in air at room temperature, though it reacts on heating.

Arsenic is stable in dry air, but tarnishes in moist air, giving first a brown and then a black tarnish. White arsenic is  $As_2O_3$ .

Antimony is less reactive, and is stable towards water and to air at room temperature.

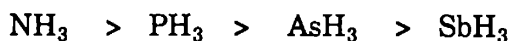
## Hydrides

- Elements of group 15 (VA), all form volatile hydrides of formula  $MH_3$ , which are all poisonous, foul smelling gases. On descending the group from  $NH_3$  to  $BiH_3$ :
  - the hydrides become increasingly difficult to prepare
  - their stability decreases
  - their reducing power decreases
  - the ease of replacing hydrogen atoms by other groups such as Cl or Me (methyl) decreases
  - Lewis-base nature (tendency to donate lone pair of electrons) decreases
  - $PH_3$  is a much weaker base than  $NH_3$ ;  $AsH_3$ ;  $SbH_3$  and  $BiH_3$  do not show any basic properties.
  - hydrides have a pyramidal structure
  - boiling point increases but  $NH_3$  is the exception due to intermolecular H-bonding**



( $BiH_3$  is very unstable)

— **bond angle decreases**



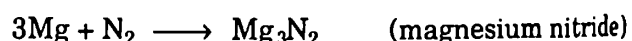
- The ionisation energy to produce  $M^{5+}$  is so large for N that it does not show +5 oxidation state. Nitrogen also differs from other elements in that it can form strong  $p\pi-p\pi$  multiple bonds and hence it produces a number of compounds which have no counter parts in other elements. Thus,  $NO_3^-$ ,  $NO_2^-$ ,  $N_3^-$  (azide),  $C \equiv N^-$ ,  $N_2O$ ,  $NO$ ,  $NO_2$ ,  $N_2O_4$ ,  $N_2O_3$ ,  $N \equiv N$ , azo and diazo compounds are formed. Oxides  $N_2O_3$  and  $N_2O_5$  are monomeric while trioxides and pentoxides of other elements are dimeric as in  $P_4O_6$  and  $P_4O_{10}$ . Phosphorus and the heavier elements of this group show  $d\pi-p\pi$  bonding.

**Illustration 1** Could the strain in the  $P_4$  molecule be reduced by using  $sp^3$  hybrid orbitals in bonding instead of pure  $p$ -orbitals? Explain.

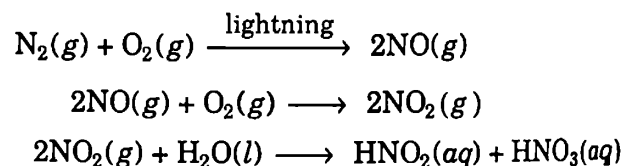
**Solution** The angle required by  $P_4$  is  $60^\circ$ . The strain would not be reduced by using  $sp^3$  hybrid orbitals because their angle is  $\sim 109^\circ$ .

## Study of Nitrogen and its Compounds

- $N_2$  makes up almost 78% of the atmosphere, and is therefore the most common gas.  $N_2$  is unreactive (inert), however it reacts with some metals forming metal nitrides which are ionic with  $N^{3-}$  ion:



- The most important compounds of nitrogen are in living things, e.g., amino acids and proteins. Among other things, the high electronegativity of nitrogen allows it to take part in H-bonding and thus helps to keep the strands of DNA together.
- Some microorganisms capture nitrogen from the atmosphere and convert it into useful compounds—a case of **nitrogen-fixation**. It involves a complicated system of biochemical reactions involving an enzyme, **nitrogenase** and **adenosine triphosphate (ATP)**. Some plants fix nitrogen by use of *Rhizobium* bacteria, which are often found in the root system. Nitrogen is also fixed by chemical reactions in the atmosphere, particularly in thunderstorms.



## DEEP Focus

- Hence, the energy released by lightning converts nitrogen into nitrogen oxides and nitric acid, which falls to earth in the rain. However, the proportion of nitrogen in the atmosphere is not continually decreasing because that lost by fixation is replaced by the decomposition of nitrogenous compounds by bacteria. This process is called **denitrification**. **Currently, the total rate of fixation exceeds the rate of return of nitrogen to the atmosphere which means that nitrogen compounds are accumulating in soil, ground water, surface water and the oceans with subsequent environmental effects, e.g.,  $NO_3^-$  occurs in ground water in higher concentration as a result of fertilisers runoff and drainage from cattle feedlots. When this water is drunk, nitrate reducing bacteria in the gastro-intestinal tract can convert  $NO_3^-$  into  $NO_2^-$ .  $NO_2^-$  interferes with the oxygen transport ability of blood, which can lead to a condition known as **methemoglobinemia**. This order can be fatal in infants.**

Nitrogen cycle is represented in Fig. 13.2.

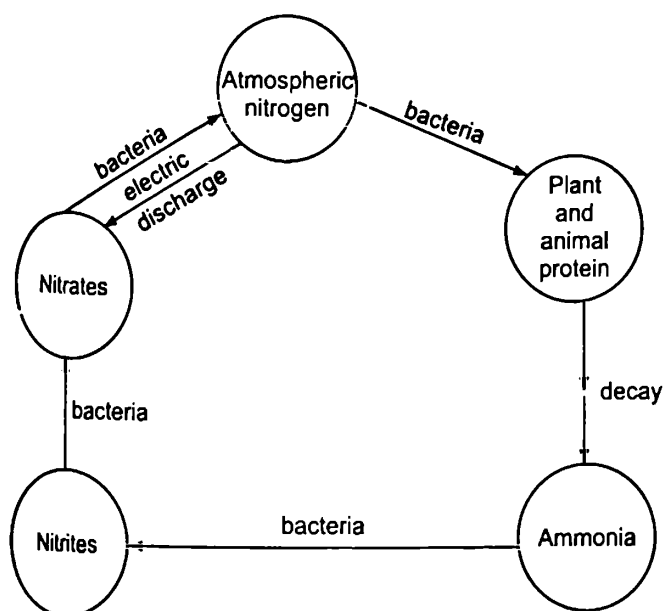


Fig. 13.2 Nitrogen cycle in nature

- On a commercial scale,  $N_2$  is obtained by the fractional evaporation of liquid air. Liquid air usually contains 50–60 per cent oxygen instead of 23 per cent in gaseous air. Since  $N_2$  and  $O_2$  differ widely in their b.p. ( $N_2 = -195^\circ C$ ,  $O_2 = -183^\circ C$ ) hence separation of  $N_2$  and  $O_2$  can be easily affected by fractional distillation.  $N_2$  thus obtained has some traces of rare gases like He and Ne.

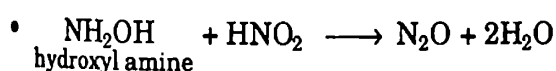
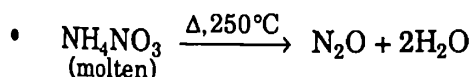
## Nitrogen Oxides

- The oxides show the wide range of oxidation numbers of N, from +1 to +5.
- All the oxides are covalent.
- All are gases at room temperature (except  $N_2O_5$  which is unstable solid at room temperature).
- The lower oxides are neutral and the higher ones are acidic. Oxides are summarised in Table 13.2.

Table 13.2 Oxides of Nitrogen

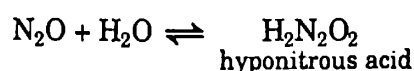
|   | Name                                       | Formula  | Oxyacid                        | Oxidation no. | Preparation                                                                       | Magnetic properties |
|---|--------------------------------------------|----------|--------------------------------|---------------|-----------------------------------------------------------------------------------|---------------------|
| 1 | Dinitrogen oxide (nitrous oxide)           | $N_2O$   | $H_2N_2O_2$ (hyponitrous acid) | +1            | $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$                                      | Diamagnetic         |
| 2 | Nitrogen monoxide (nitric oxide)           | $NO$     | —                              | +2            | $3Cu + 8HNO_3 \xrightarrow[\text{dil.}]{\Delta} 3Cu(NO_3)_2 + 2NO + 4H_2O$        | Paramagnetic        |
| 3 | Nitrogen dioxide                           | $NO_2$   | —                              | +4            | $2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$                             | Paramagnetic        |
| 4 | Dinitrogen tetroxide                       | $N_2O_4$ | —                              | +4            | $Cool\ NO_2, \ N_2O_4 \xrightleftharpoons[\text{cool}]{\Delta} 2NO_2$             | Diamagnetic         |
| 5 | Dinitrogen trioxide (nitrogen sesquioxide) | $N_2O_3$ | $HNO_2$                        | +3            | $NO + NO_2 \longrightarrow N_2O_3$<br>$2HNO_2 \xrightarrow{\Delta} N_2O_3 + H_2O$ | Diamagnetic         |
| 6 | Dinitrogen pentoxide                       | $N_2O_5$ | $HNO_3$                        | +5            | $2HNO_3 \xrightarrow{P_2O_5} N_2O_5 + H_2O$                                       | Diamagnetic         |

## Nitrous oxide ( $N_2O$ )



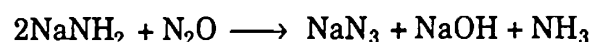
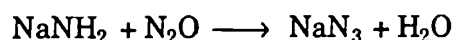
It is stable, relatively unreactive colourless gas, it is a neutral oxide.

It is soluble in water (1:1 by volume), but solution is neutral probably the following equilibrium lies in left-hand side

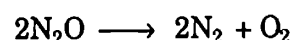


It may be taken as anhydride of  $H_2N_2O_2$

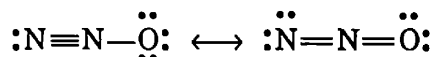
- It forms sodium azide on reaction with  $NaNH_2$  :



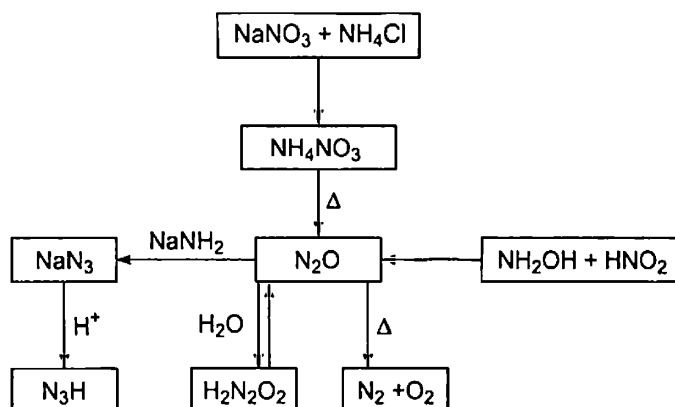
- $N_2O$  resembles molecular oxygen ( $O_2$ ) in that it supports combustion. It does so because it decomposes to molecular nitrogen and molecular oxygen when heated



- The molecule is linear as would be expected for a triatomic molecule with 16 outer shell electrons (as for  $CO_2$ ).

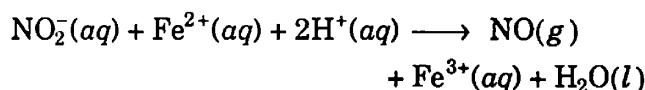


- The largest use of  $\text{N}_2\text{O}$  is as a propellant for whipped ice-cream. Because it has no taste, and is non-toxic, it meets the strict food and health regulations.
- $\text{N}_2\text{O}$  is also used as an anaesthetic, particularly by dentists. It is also called **laughing gas**, because small amounts cause **euphoria**.

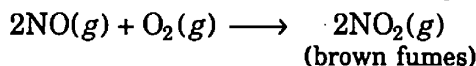


## Nitric Oxide (NO)

- $\text{N}_2 + \text{O}_2 \longrightarrow 2\text{NO}$
- $3\text{Cu} + 8\text{HNO}_3 \xrightarrow{\text{dil}} 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
- $2\text{HNO}_2 + 2\text{I}^- + 2\text{H}^+ \longrightarrow 2\text{NO} + \text{I}_2 + 2\text{H}_2\text{O}$
- NO can be prepared in the laboratory by reacting sodium nitrite ( $\text{NaNO}_2$ ) with a reducing agent such as  $\text{Fe}^{2+}$  in an acidic medium



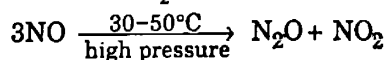
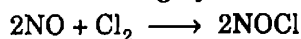
- $2\text{NO}_3^- + 6\text{Hg} + 8\text{H}^+ \longrightarrow 3\text{Hg}_2^{2+} + 2\text{NO} + 4\text{H}_2\text{O}$
- Lighting also contributes to the atmospheric concentration of NO. Exposed to air, nitric oxide quickly forms brown nitrogen dioxide gas:



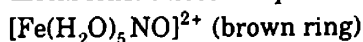
Nitrogen dioxide is a major component of smog.

## DEEP Focus

- NO is an odd-electron molecule; alternately we can say it is a free-radical. Hence it is highly reactive:

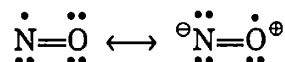


NO readily forms coordination complexes with transition metal ions. These complexes are called **nitrosyls**.

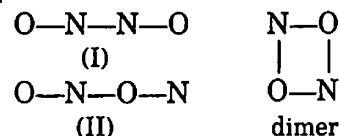


- Bond-order is 2.5 (as described by M.O. theory) and bond length is  $1.15\text{ \AA}$  which is intermediate between a double bond and a triple bond.

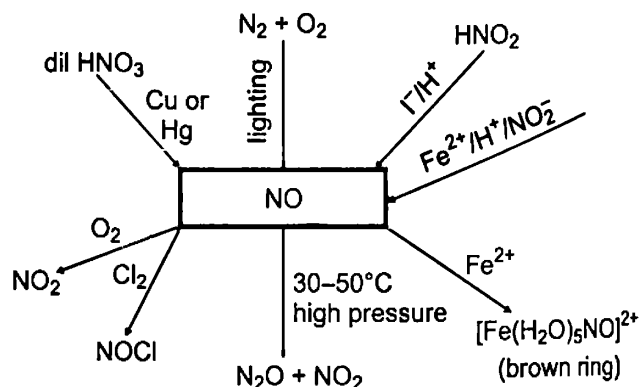
- It can be represented by the following resonance structures:



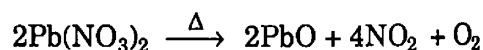
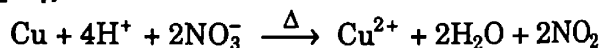
Due to one unpaired electron (total 11 valence electrons) it is paramagnetic. In solid and liquid state it dimerises forming  $\text{N}_2\text{O}_2$  and paramagnetism disappears.



II is asymmetrical and is formed as a red solid in the presence of HCl.

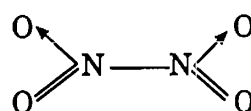
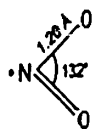


## Nitrogen dioxide ( $\text{NO}_2$ ), dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ )



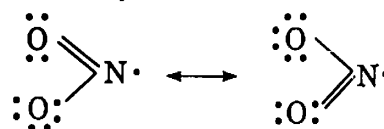
On condensation,  $\text{NO}_2$  is obtained as a pale liquid and ultimately a colourless solid ( $\text{N}_2\text{O}_4$  due to dimerisation).

- $\text{NO}_2$  is paramagnetic due to unpaired electron but in dimer formation paramagnetism disappears due to pairing of unpaired electrons



This reaction occurs in both the gas phase and the liquid phase.

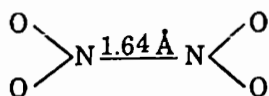
- It is represented by resonance structures:



- $\text{NO}_2$  molecule is angular with an O—N—O angle of  $132^\circ$  and N—O bond length of  $1.20\text{ \AA}$  (which is intermediate between a single and a double bond).

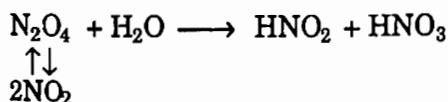
**DEEP Focus**

- $\text{N}_2\text{O}_4$  has planar structure studied by X-ray



N—N bond length (1.64 Å) in  $\text{N}_2\text{O}_4$  is about 20% larger than the usual N—N single bond. We can think of the positive charge formed on the adjacent N atoms which causes repulsion and thus increases the bond length.

- $\text{N}_2\text{O}_4$  is a mixed anhydride as indicated by its reaction with  $\text{H}_2\text{O}$  when  $\text{HNO}_2$  (nitrous acid) and  $\text{HNO}_3$  (nitric acid) are formed

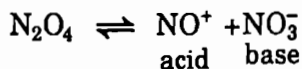


The  $\text{HNO}_2$  formed decomposes to give NO and  $\text{NO}_2$



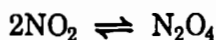
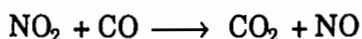
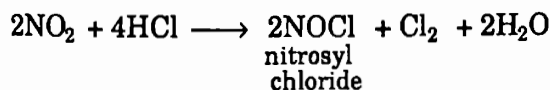
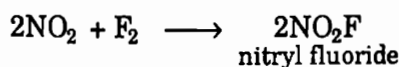
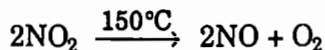
Thus moist  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  gases are strongly acidic.

- Liquid  $\text{N}_2\text{O}_4$  is useful as a non-aqueous solvent and self-ionises as



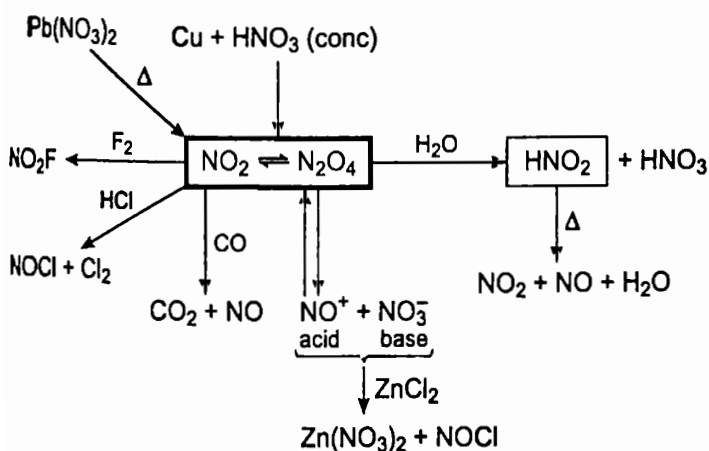
Thus,  $\text{ZnCl}_2 + 2\text{N}_2\text{O}_4 \longrightarrow 2\text{NOCl} + \text{Zn}(\text{NO}_3)_2$

- $\text{NO}_2$ — $\text{N}_2\text{O}_4$  system is a strong oxidising agent

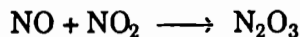


$\text{N}_2\text{O}_4$  solidifies at  $-11.2^\circ\text{C}$  and is colourless.

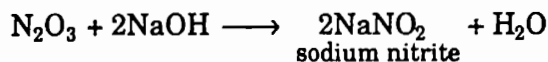
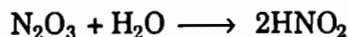
As the temperature increases, proportion of brown  $\text{NO}_2$  increases and the colour of the liquid darkens. At around  $140^\circ\text{C}$ , the mixture is almost entirely  $\text{NO}_2$ .

**Dinitrogen Trioxide ( $\text{N}_2\text{O}_3$ )**

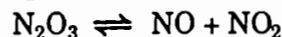
- It is obtained by condensing equimolar amount of NO and  $\text{NO}_2$  together, or by reacting NO with  $\text{O}_2$  in a fixed ratio.



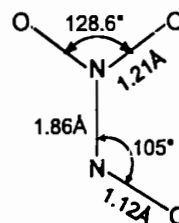
- It is an acidic oxide and is the anhydride of  $\text{HNO}_2$



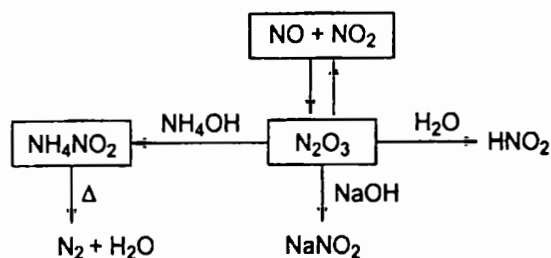
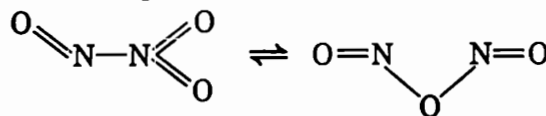
- It is an intensely blue liquid or a pale blue solid. It exists only at low temperature and readily dissociates to give NO and  $\text{NO}_2$



- The  $\text{N}_2\text{O}_3$  molecule has an  $\text{O}_2\text{N}$ —NO structure in the gas phase and at low temperature, with an extremely long (1.86 Å) N—N bond which is consistent with its easy dissociation.



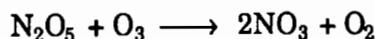
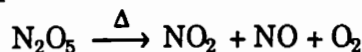
Two interconvertible structures (in presence of light radiations of a particular wavelength) are assigned to it.

**Dinitrogen Pentoxide ( $\text{N}_2\text{O}_5$ )**

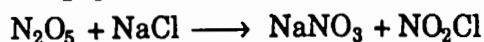
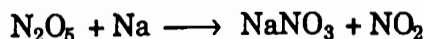
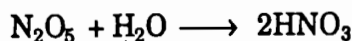
- $2\text{HNO}_3 \xrightarrow[\text{low temp.}]{\text{P}_2\text{O}_5} \text{N}_2\text{O}_5 + \text{H}_2\text{O}$

Thus  $\text{N}_2\text{O}_5$  is the anhydride of  $\text{HNO}_3$ .

- It is colourless deliquescent solid and highly reactive.
- In the gaseous phase :

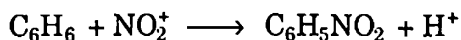
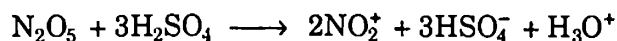


- In solid state :

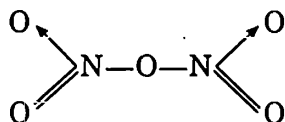




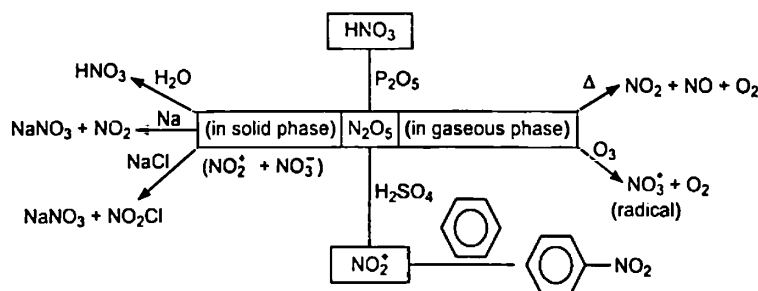
- With conc.  $\text{H}_2\text{SO}_4$ , it forms  $\text{NO}_2^+$  (nitronium ion) which can attack benzene nucleus forming nitrobenzene



- X-ray diffraction shows that solid  $\text{N}_2\text{O}_5$  is ionic  $\text{NO}_2^+ \text{NO}_3^-$  (nitronium nitrate). In the solution and gaseous phase, it is covalent with structure :

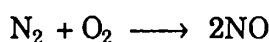


Each N atom is  $sp^2$ -hybridised.



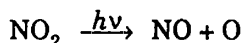
## Nitrogen Oxides and Air Pollution

Collectively, nitrogen oxides are often given the symbol  $\text{NO}_x$ . Two of them, NO and  $\text{NO}_2$  are of special importance in environmental chemistry, causing considerable amount of air pollution. They are given off in car exhaust fumes and when fossil fuels are burnt, as well as being made during thunderstorms. In each case NO is made and then  $\text{NO}_2$ .



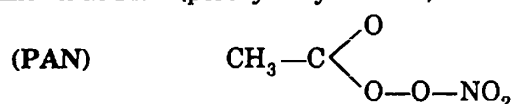
### DEEP Focus

$\text{NO}_2$  is more unpleasant and gives rise to acid rain and also takes part in photochemical reactions forming smog. The photons making up sunlight can cause the  $\text{NO}_2$  molecules to fall apart, releasing oxygen atoms:



Oxygen atoms are extremely reactive and will attack other molecules, especially those in car exhaust fumes. For examples hydrocarbons that escape combustion can be changed into aldehydes. The oxygen atoms can also react with  $\text{O}_2$  to form  $\text{O}_3$ .

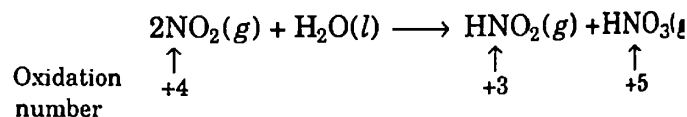
$\text{NO}_2$  is also involved in the production of one of the most unpleasant of all chemicals present in photochemical smog. It is known as PAN (peroxyacetyl nitrate):



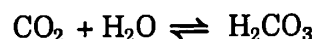
Its presence in the atmosphere irritates eyes and lungs and generally makes breathing difficult.

**Illustration 1** What is difference in the nature of the products obtained when  $\text{CO}_2(\text{g})$  and  $\text{NO}_2(\text{g})$  are dissolved separately in water?

**Solution**  $\text{NO}_2$  is an acidic oxide; it reacts rapidly with cold water to form both nitrous acid,  $\text{HNO}_2$ , and nitric acid,  $\text{HNO}_3$

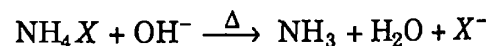


This is a disproportionation reaction in which the oxidation number of nitrogen changes from +4 (in  $\text{NO}_2$ ) to +3 (in  $\text{HNO}_2$ ) and +5 (in  $\text{HNO}_3$ ). This reaction is quite different from that between  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in which only one acid ( $\text{H}_2\text{CO}_3$ , carbonic acid) is formed without change in oxidation number of carbon



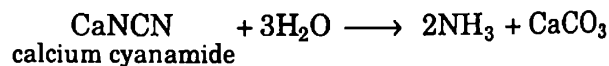
## Ammonia ( $\text{NH}_3$ )

- $\text{NH}_3$  is formed by decomposing  $\text{NH}_4^+$  salts with a base

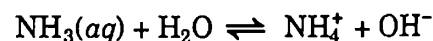


$$K_{298} = 10^3 \text{ atm}^{-2}$$

This is the basis of the Haber process and is carried out at  $400\text{--}500^\circ\text{C}$  and at a pressure of  $10^2\text{--}10^3 \text{ atm}$  in the presence of a catalyst.



- Ammonia is extremely soluble in water. Although an aqueous solution is generally referred to as solution of weak base  $\text{NH}_4\text{OH}$ , undissociated  $\text{NH}_4\text{OH}$  does not exist. The solutions are best described as  $\text{NH}_3(\text{aq})$  with equilibrium :

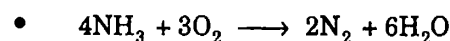


$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} \text{ mol L}^{-1}$$

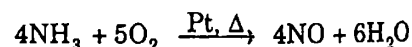
- $\text{NH}_3$  is colourless, pungent and quite poisonous gas (b.p  $-33.35^\circ\text{C}$ )

### DEEP Focus

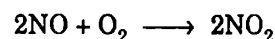
#### Oxidation



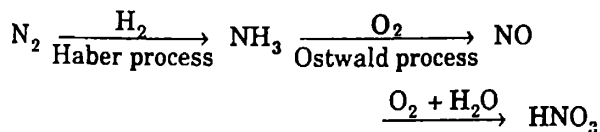
This reaction is thermodynamically favoured under normal conditions. However, at  $750\text{--}900^\circ\text{C}$ , in the presence of Pt catalyst, NO is formed.



Thus NO can be converted into  $\text{NO}_2$  which in turn into  $\text{HNO}_3$



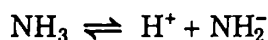
Thus the sequence in industrial utilisation of atmospheric nitrogen is as follows:



- Liquid  $\text{NH}_3$  resembles water in its physical behaviour, being highly associated *via* strong hydrogen bonding. Like  $\text{H}_2\text{O}$  it also self-ionises:

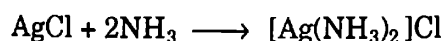


or



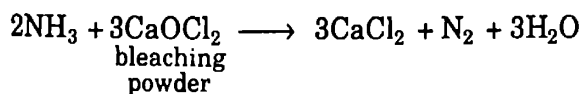
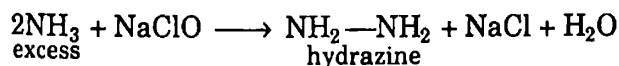
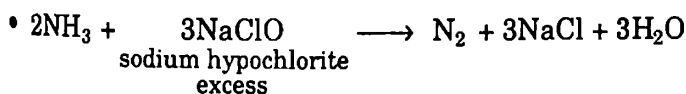
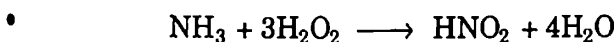
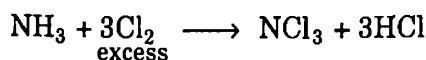
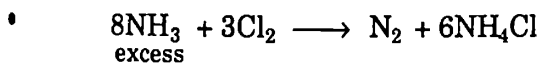
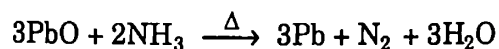
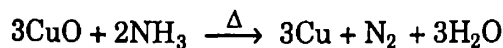
### As a Ligand

- Because  $\text{NH}_3(l)$  has a much lower dielectric constant than water, it is a better solvent for organic compounds but generally a poorer one for ionic inorganic compounds. But complex formation by  $\text{NH}_3$  (as ligand) is better than that by  $\text{H}_2\text{O}$ .  $\text{AgCl}$  is insoluble in  $\text{H}_2\text{O}$  but soluble in  $\text{NH}_3$  due to complex formation :

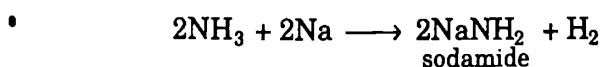


### Reducing Nature

- $\text{NH}_3$  can reduce oxides into metal :



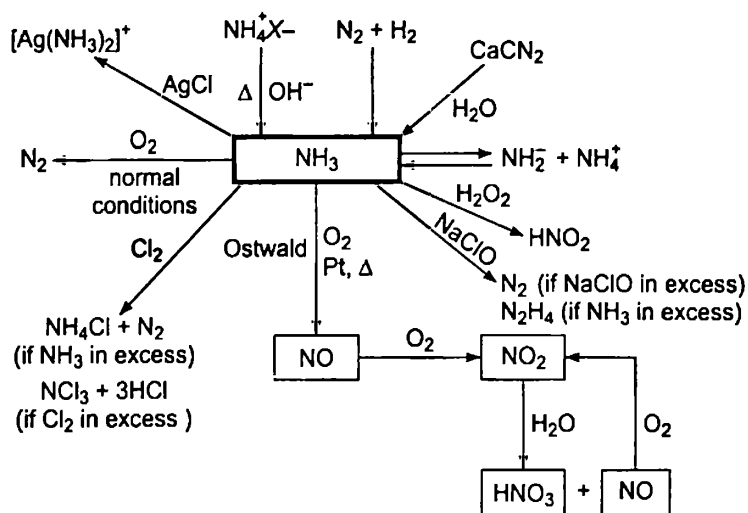
### Solvated Electrons



Dilute solutions of alkali metals in liquid  $\text{NH}_3$  are dark blue in colour and the main species are solvated metal ions and solvated electrons.

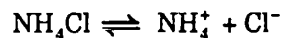
### Test

- $2\text{K}_2\text{HgI}_4 + \text{NH}_3 + 3\text{KOH} \longrightarrow \text{H}_2\text{NHgOHgI} \downarrow$   
Nessler's reagent      iodide of Millon's base (brown ppt.)  
 $+ 7\text{KI} + 2\text{H}_2\text{O}$
- $\text{CaSO}_4 + 2\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$
- $2\text{NH}_3 + \text{CO}_2 \rightleftharpoons \text{NH}_2\text{COONH}_4 \xrightarrow{\Delta} \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O}$   
ammonium carbamate      urea

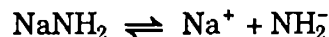


### DEEP Focus

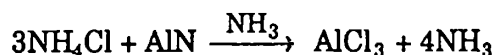
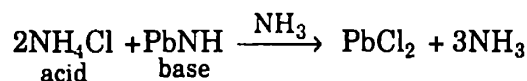
- Liquid ammonia functions as a good solvent for many substances and many types of reactions. **All those substances which dissolve in liquid  $\text{NH}_3$  to give  $\text{NH}_4^+$  ions are acids** and those which give amides,  $\text{NH}_2^-$  ions are bases.  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$  are acids in liquid  $\text{NH}_3$  due to existence of  $\text{NH}_4^+$  ions.



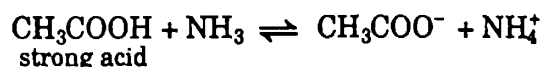
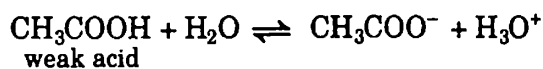
$\text{NaNH}_2$  is a base in liquid  $\text{NH}_3$  due to existence of  $\text{NH}_2^-$  ion:



Acid-base neutralisation reaction in liquid  $\text{NH}_3$  can be thus represented as,



- Acids which are weak in water will be highly acidic in liquid  $\text{NH}_3$ :

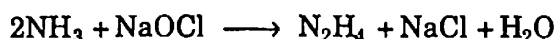


## Hydrazine (N<sub>2</sub>H<sub>4</sub>)

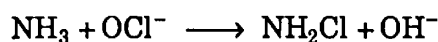
### Preparation

#### Raschig Process

It is obtained by controlled oxidation of NH<sub>3</sub> (in excess) by alkaline solution of sodium hypochlorite (NaOCl):

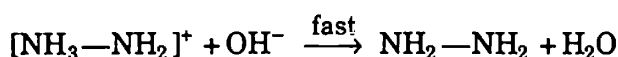
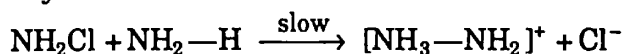


Reaction involves rapid formation of chloramine (NH<sub>2</sub>Cl)

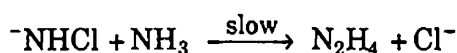
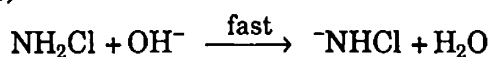


NH<sub>2</sub>Cl changes to N<sub>2</sub>H<sub>4</sub> by path I or path II

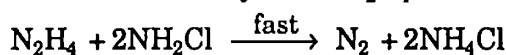
**Path I** It involves nucleophilic attack of NH<sub>3</sub> followed by neutralisation with alkali



**Path II** There is formation of chloramide ion <sup>-</sup>NHCl (in fast step) followed by nucleophilic attack of NH<sub>3</sub> (in slow step)



A side reaction decreases yield of N<sub>2</sub>H<sub>4</sub>



The reaction is catalysed by traces of heavy metal ions (e.g., Cu<sup>2+</sup>). Addition of gelatin or glue suppresses the side reaction by complexing the metal ions and yield of hydrazine is increased.

Industrially and laboratory method involve the same type of reactants. Urea may replace ammonia.

### Properties

- Colourless fuming liquid with faint ammoniacal odour.

Melting point : 20°C

Boiling point : 113.5°C

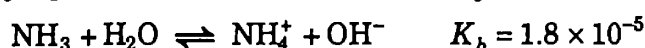
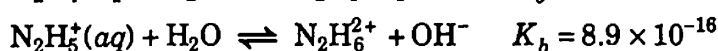
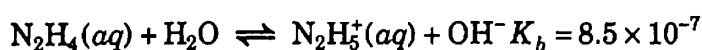
Density : 1 g/cm<sup>3</sup> at 25°C

Dielectric constant : 51.7 at 25°C

$\Delta H_f^\circ$  : 50.6 kJ mol<sup>-1</sup> (an endothermic compound)

$\Delta G_f^\circ$  : 149.0 kJ mol<sup>-1</sup>

- Pure hydrazine and its aqueous solution are kinetically stable in spite of its endothermic nature.
- Basic Nature** It is a weaker base than NH<sub>3</sub> but its behaviour is **bifunctional**.



Hydrazinium salts of N<sub>2</sub>H<sub>5</sub><sup>+</sup> are stable in water but those of N<sub>2</sub>H<sub>6</sub><sup>2+</sup> are hydrolysed in aqueous solution.

Such salts as N<sub>2</sub>H<sub>6</sub><sup>2+</sup> are less soluble than those of N<sub>2</sub>H<sub>5</sub><sup>+</sup> and may be crystallised in presence of acid.

These series of salts are formed with H<sub>2</sub>SO<sub>4</sub>

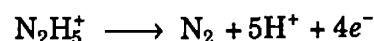
(N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>SO<sub>4</sub> with N<sub>2</sub>H<sub>5</sub><sup>+</sup> cation

(N<sub>2</sub>H<sub>6</sub>)SO<sub>4</sub> with N<sub>2</sub>H<sub>6</sub><sup>2+</sup> cation

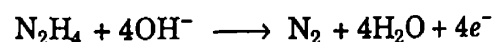
(N<sub>2</sub>H<sub>6</sub>)(HSO<sub>4</sub>)<sub>2</sub> with N<sub>2</sub>H<sub>6</sub><sup>2+</sup> cation

- Reducing Nature** : N<sub>2</sub>H<sub>4</sub> is oxidised to N<sub>2</sub> and thus it is a better reducing agent.

**In acidic medium**



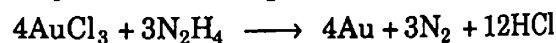
**In basic medium**



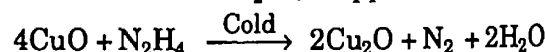
$$\text{Equivalent mass} = \frac{\text{molar mass}}{4}$$

$$= \frac{32}{4} = 8.0 \text{ g equivalent}^{-1}$$

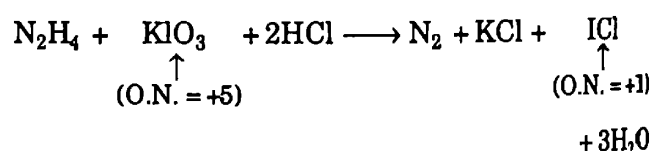
- AuCl<sub>3</sub> is reduced to N<sub>2</sub>



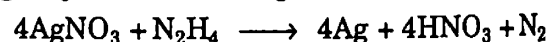
- CuO is reduced to Cu<sub>2</sub>O (red ppt)



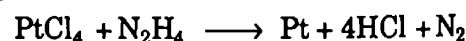
- IO<sub>3</sub><sup>-</sup> is reduced to I<sup>-</sup>



- AgNO<sub>3</sub> is reduced to Ag

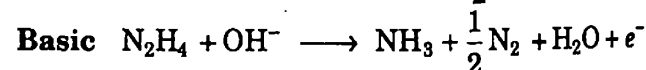
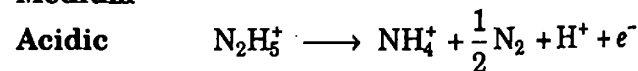


- PtCl<sub>4</sub> is reduced to Pt

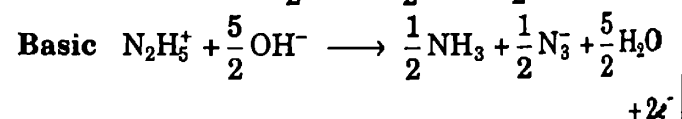
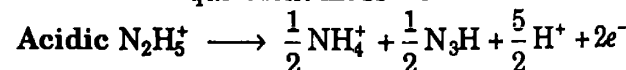


N<sub>2</sub>H<sub>4</sub> is oxidised to NH<sub>3</sub> and N<sub>2</sub> or N<sub>3</sub><sup>-</sup>

**Medium**



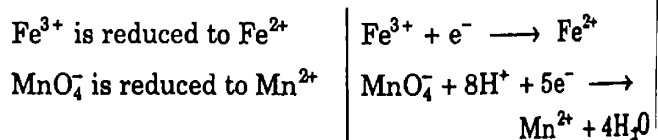
Equivalent mass = molar mass



$$\text{Equivalent mass} = \frac{\text{molar mass}}{2}$$

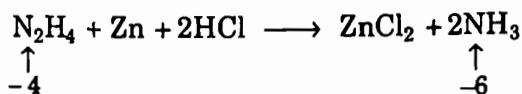
Fe<sup>3+</sup> is reduced to Fe<sup>2+</sup>

MnO<sub>4</sub><sup>-</sup> is reduced to Mn<sup>2+</sup>



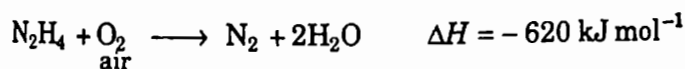
## Oxidising Nature

In presence of a powerful reducing agent (as Zn/HCl), it is an oxidising agent



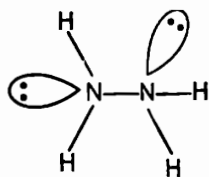
$$\text{Equivalent mass of N}_2\text{H}_4 = \frac{\text{molar mass}}{2}$$

**As a Rocket Fuel** Hydrazine being an endothermic compound burns rapidly and completely in air with evolution of heat



Thus,  $\text{N}_2\text{H}_4$  is used as a rocket fuel in guided missile, space shuttles and lunar missions.

### Structure



Each N-atom is  $sp^3$ -hybridised and tetrahedrally surrounded by one nitrogen, two hydrogen and one lone pair of electrons. The molecule has a *gauche* conformation with an angle of rotation of  $95^\circ$  from a purely eclipsed position.

## Uses

- As a rocket fuel; methyl derivatives  $\text{MeNHNH}_2$  and  $\text{Me}_2\text{NNH}_2$  are also used in combination with it. Oxidants are  $\text{O}_2$  (liquid),  $\text{N}_2\text{O}_4$  or  $\text{H}_2\text{O}_2$ .
- As a reducing agent to prepare copper and silver mirror; to prepare platinum metal.
- Isonicotinic hydrazine ( $\text{C}_5\text{H}_4\text{NCONHNH}_2$ ) is an antitubercular drug.

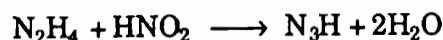
## Similarity Between Hydrazine and Hydrogen Peroxide

|                     | $\text{N}_2\text{H}_4$                                                              | $\text{H}_2\text{O}_2$                                                                 |
|---------------------|-------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|
| 1. Structures       |                                                                                     |                                                                                        |
| 2. Association      | Form liquid and solid through hydrogen-bonding                                      |                                                                                        |
| 3. Hybridisation    | N-atom is $sp^3$ -hybridised                                                        | O-atom is $sp^3$ -hybridised                                                           |
| 4. Decomposition    | $3\text{N}_2\text{H}_4 \longrightarrow \text{N}_2 + 4\text{NH}_3$                   | $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$               |
| 5. Oxidising nature | $\text{N}_2\text{H}_5^+ + 3\text{H}^+ + 2\text{e}^- \longrightarrow 2\text{NH}_4^+$ | $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow 2\text{H}_2\text{O}$ |
| 6. Reducing nature  | $\text{N}_2\text{H}_5^+ \longrightarrow \text{N}_2 + 5\text{H}^+ + 4\text{e}^-$     | $\text{H}_2\text{O}_2 \longrightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$          |

## Hydrogen Azide (Hydrazoic acid) $\text{N}_3\text{H}$

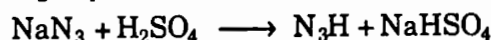
### Preparation

- By oxidation of aqueous hydrazine with nitrous acid

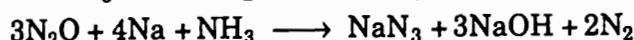
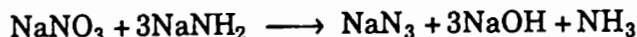
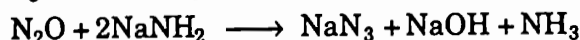


Oxidising agent can be  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$ ,  $\text{ClO}_3^-$  etc.

- By careful distillation of sodium azide ( $\text{NaN}_3$ ) with dilute  $\text{H}_2\text{SO}_4$

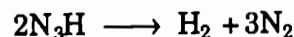


$\text{NaN}_3$  is formed by

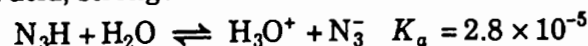


### Properties

- Colourless liquid, boiling point  $37^\circ\text{C}$ . The liquid and vapour are deadly poisonous and explode on heating



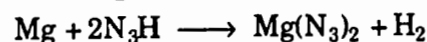
- Weak acid, stronger than acetic acid



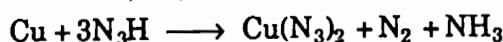
$$K_a' = 1.8 \times 10^{-5}$$

$$(K_a > K_a')$$

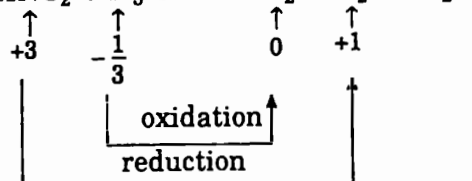
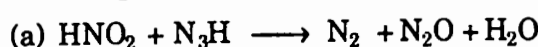
- $\text{N}_3\text{H}$  dissolves Mg forming  $\text{H}_2$



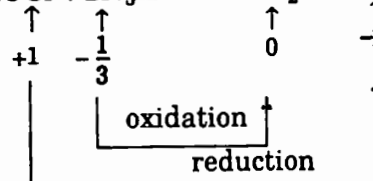
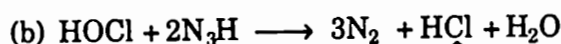
- Metals like Cu, Zn, Fe form  $\text{NH}_3$  and  $\text{N}_2$  with  $\text{N}_3\text{H}$



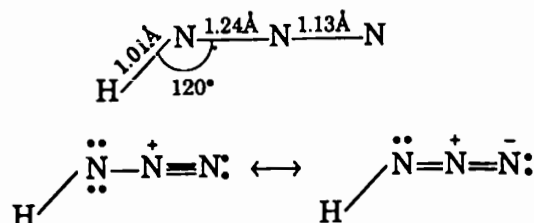
- Reducing nature



$\text{N}_3\text{H}$  may be estimated by titration with  $\text{NaNO}_2$  solution using  $\text{FeCl}_3$  as an indicator  $\text{N}_3\text{H}$  gives red colour with  $\text{FeCl}_3$ .



**Structure** The azide ion has very much similarity with halide ions and cyanide ion and is termed as **pseudo halide**.

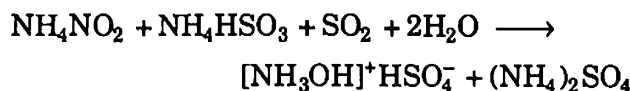


## Hydroxyl Amine (NH<sub>2</sub>OH)

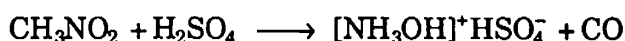
### Preparation

It is stable in the form of acid salt as [NH<sub>3</sub>OH]<sup>+</sup>Cl<sup>-</sup> or [NH<sub>3</sub>OH]<sup>+</sup>HSO<sub>4</sub><sup>-</sup>

1. NH<sub>2</sub>OH in the form of salt is formed when ammonium nitrite (NH<sub>4</sub>NO<sub>2</sub>) reacts with ammonium hydrogen sulphite (NH<sub>4</sub>HSO<sub>3</sub>) in presence of sulphur dioxide (SO<sub>2</sub>).



2. Methyl nitrite (CH<sub>3</sub>NO<sub>2</sub>) changes to [NH<sub>3</sub>OH]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> on reaction with H<sub>2</sub>SO<sub>4</sub>



### Properties

1. Pure NH<sub>2</sub>OH is colourless, odourless deliquescent crystals — melting point = 33°C

boiling point = 58°C at 72 mmHg

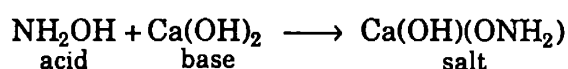
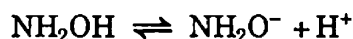
2. Dielectric constant = 78

highly soluble in water and alcohol but slightly in ether or benzene.

3. Its aqueous solution is less basic than NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub>



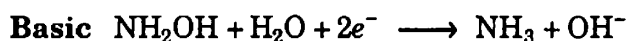
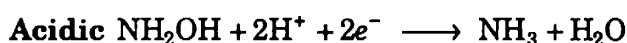
4. In absence of H<sub>2</sub>O, it also behaves as a weak acid



### 5. NH<sub>2</sub>OH as an oxidising agent

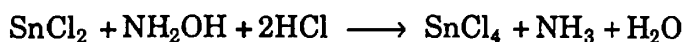
NH<sub>2</sub>OH can be reduced to NH<sub>3</sub> hence it can be used as an oxidising agent

#### Medium

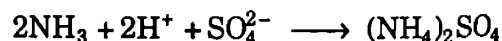
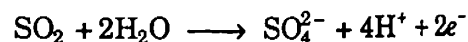


$$\text{Equivalent mass} = \frac{\text{molar mass}}{2}$$

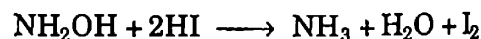
- (a) SnCl<sub>2</sub> is oxidised to SnCl<sub>4</sub> in acidic medium



- (b) SO<sub>2</sub> is oxidised to SO<sub>4</sub><sup>2-</sup> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is the end product.



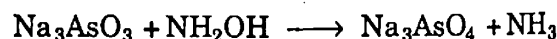
- (c) HI is oxidised to I<sub>2</sub>



- (d) Fe(OH)<sub>2</sub> is oxidised to Fe(OH)<sub>3</sub> in basic medium

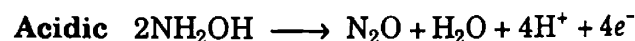


- (e) Na<sub>3</sub>AsO<sub>3</sub> (sodium argenite) is oxidised to Na<sub>3</sub>AsO<sub>4</sub> (sodium argenate) in basic medium



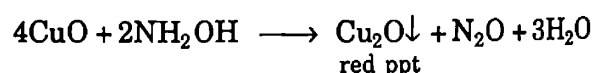
### 6. NH<sub>2</sub>OH as a reducing agent

#### Medium

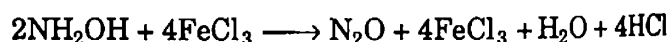


$$\text{Equivalent mass} = \frac{\text{molar mass}}{4}$$

- (a) CuO(II) is reduced to Cu<sub>2</sub>O(I)

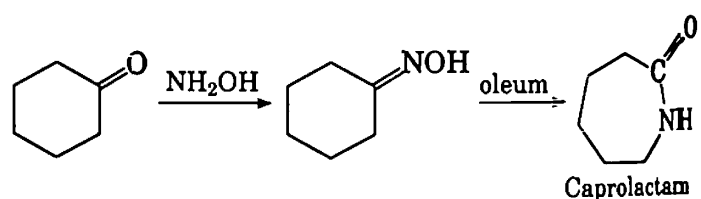


- (b) Fe<sup>3+</sup>(III) is reduced to Fe<sup>2+</sup>(II)



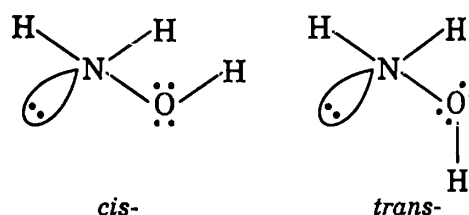
### Uses

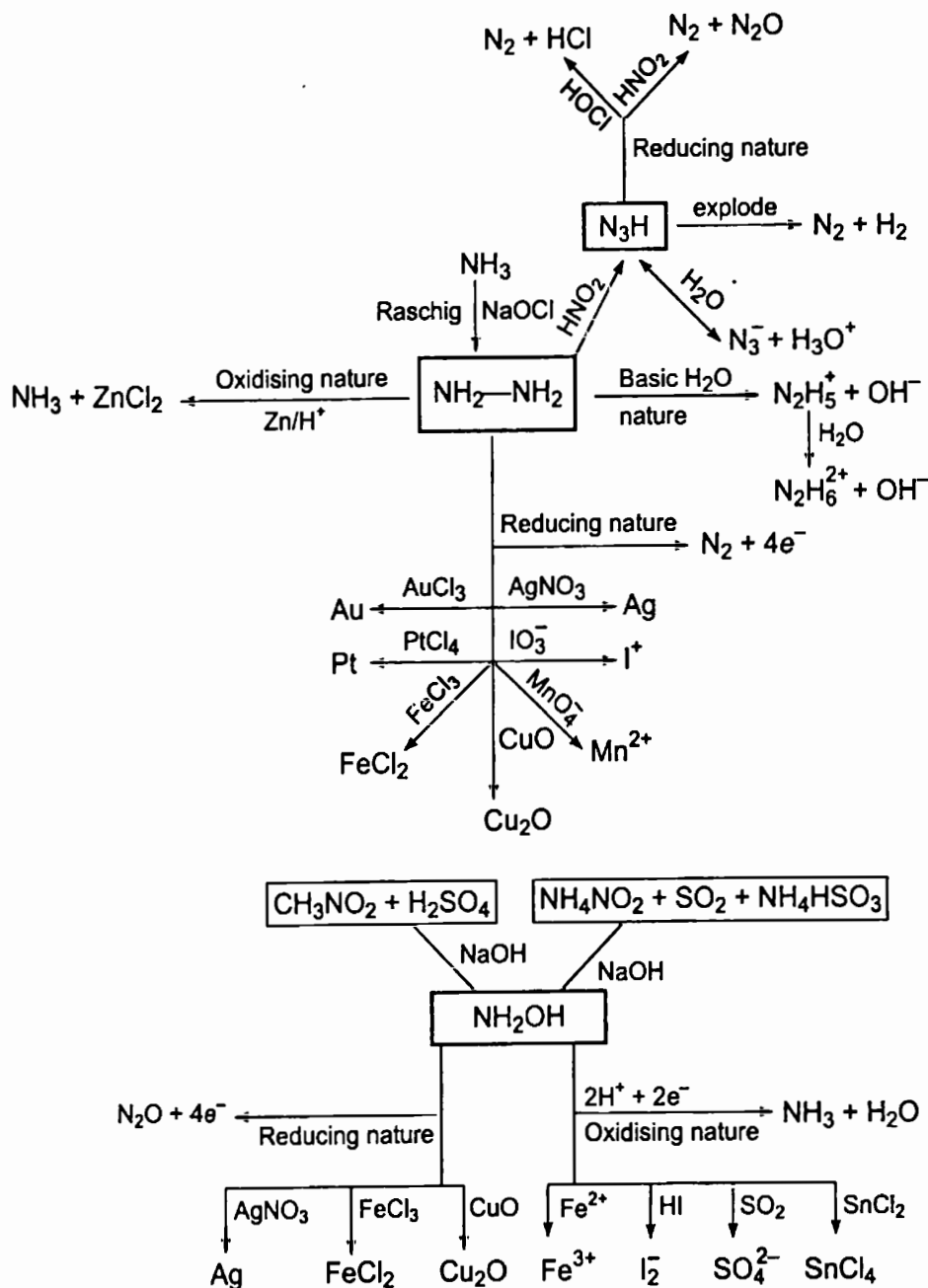
- (i) As a reducing agent-antioxidant in photographic developers and reduction of Cu(II) in the dyeing of acrylic fibres.
- (ii) In the preparation of caprolactam (as intermediate in the manufacture of nylon-6)



### Structure

N-atom is sp<sup>3</sup>-hybridised with one lone pair of electrons. The N—O bond distance is 1.47 Å which corresponds to single bond.





## Target Practice 1

1. Boiling points of different hydrides ( $\text{MH}_3$ ) of group 15 elements have been represented in the graphical form

Hydrides ( $\text{MH}_3$ ) are

A ..... B .....

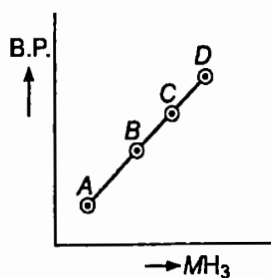
C ..... D .....

Bond angle ( $\text{H—M—H}$ ) is

maximum in .....

Basic nature is maximum in .....

2. In qualitative inorganic analysis of basic radicals, solution is prepared in dil. HCl and then diluted with  $\text{H}_2\text{O}$  before  $\text{H}_2\text{S}$  gas is passed. Orange turbidity appeared in one case on dilution.



- (a) What do you conclude about basic radical? .....
- (b) Turbidity dissolves when we add .....
3. Write full form of ATP .....
4. When there is thunderstorm accompanying lighting and rain, some oxoacids are formed.  
Oxoacids are .....  
and chemical reactions taking place are .....
5. Nitrite interferes in the oxygen transport ability of blood causing a disease known as .....
6. NO is a free radical. What is  
(a) bond order? .....  
(b) number of unpaired electrons? .....  
(c) bond length between N and O? .....

7.  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  is formed by charge-transfer mechanism. Explain it.

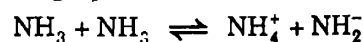
What is magnetic moment of iron in it?

8.  $\text{N}_2\text{O}_5$  is said to be ionic in solid state. Write the cation and anion in it and hybridised state of each N atom.

| Species |     | Hybridisation |
|---------|-----|---------------|
| Cation  | ... | ...           |
| Anion   | ... | ...           |

9. In presence of conc.  $\text{H}_2\text{SO}_4$ ,  $\text{N}_2\text{O}_5$  can be used as the nitrating agent. Explain the formation of the intermediate.

10. Consider following equilibrium

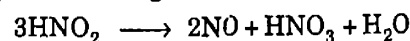


- (a) it is called .....  
 (b) based on the above equilibrium,  $\text{NH}_3$  is .....  
 (c) ionic product of above equilibrium is written as .....

11.  $\text{Cl}_2$  is passed into  $\text{NH}_3$ . What are the products

- (a) when  $\text{Cl}_2$  is in excess .....?  
 (b) when  $\text{NH}_3$  is in excess .....?

12. What is type of following reaction?



## Answers

1. A :  $\text{PH}_3$  B :  $\text{AsH}_3$  C :  $\text{NH}_3$  D :  $\text{SbH}_3$

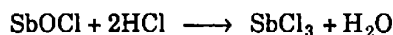
$\text{NH}_3$  (bond angle maximum)

$\text{NH}_3$  (basic nature maximum)

2. (a)  $\text{Sb}^{3+}$

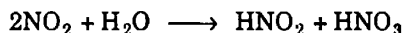
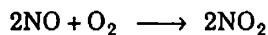
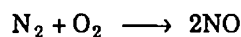


- (b)  $\text{HCl}$



3. Adenosine tri-phosphate

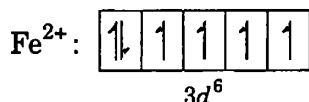
4.  $\text{HNO}_2$ ,  $\text{HNO}_3$



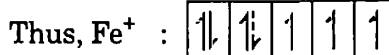
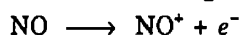
5. Methemoglobinemia.

6. (a) 2.5 (b) 1 (c) 1.15 Å

7.  $\text{Fe} : [\text{Ar}] 4s^2 3d^6$



$\text{NO}$  donates its electrons to  $\text{Fe}^{2+}$  (charge transfer)



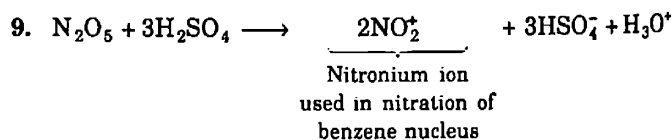
Thus, in  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  there is positive charge on Fe as well as on NO.

Unpaired electron in  $\text{Fe}^+ = 3 = N$

$$\text{Thus, magnetic moment} = \sqrt{N(N+2)} \text{ BM} \\ = \sqrt{15} \text{ BM}$$

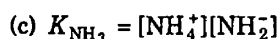
8. Cation :  $\text{NO}_2^+$  —  $sp$

Anion :  $\text{NO}_3^-$  —  $sp^2$

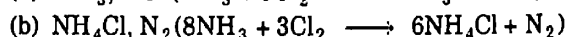


10. (a) Self ionisation (autoprotolysis in which  $\text{NH}_3$  is proton donor as well as proton acceptor).

(b) Amphiprotic.



11. (a)  $\text{NCl}_3$ ,  $\text{HCl}$  ( $\text{NH}_3 + 3\text{Cl}_2 \longrightarrow \text{NCl}_3 + 3\text{HCl}$ )



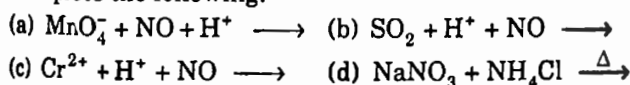
12. It is a disproportionation reaction.

## Practice Exercise 1

- Give examples of compounds of N with oxidation number -3 to +5.
- Nitrogen does not form  $\text{NCl}_5$  or  $\text{NF}_5$  but phosphorus can. Explain.
- $\text{P}_4$  exists but  $\text{N}_4$  does not;  $\text{N}_2$  exists but  $\text{P}_2$  does not. Explain.
- What happens when  $\text{PH}_3$  reacts with  
 (a) Aqueous  $\text{Ag}^+$  (b) Aqueous  $\text{Cu}^{2+}$  (c)  $\text{O}_2$
- There are two colourless solutions (A) and (B) both give white ppt with  $\text{AgNO}_3$ ; ppt dissolves in aq  $\text{NH}_3$ . Also (A) on reaction with  $\text{H}_2\text{O}$  gives orange turbidity while (B) gives white turbidity. Identify (A) and (B). Suggest the reagent that can dissolve turbidity.

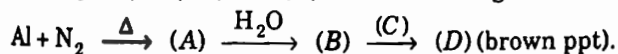
- $\text{N}_2$  can be obtained by  
 (a) passing  $\text{NH}_3$  over red-hot copper (II) oxide  
 (b) heating  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ .  
 (c) passing  $\text{NH}_3$  into suspension of bleaching powder  
 Write a balanced equation for each preparation.
- Some farmers feel that lightning helps produce a better crop. What is the scientific basis for this belief?
- $\text{NO}$  often acts as a three electron donor in contrast to most ligands which donate two electrons. What happens when  $\text{NO}$  replaces three CO in  $[\text{Fe}(\text{CO})_5]$  and six CO in  $[\text{Cr}(\text{CO})_6]$ ?
- Mixture of  $\text{KNO}_3$  and  $\text{KNO}_2$  can oxidise  $\text{Cr}_2\text{O}_3$  to  $\text{CrO}_4^{2-}$ . Write chemical equation to represent change.

10. Complete the following:

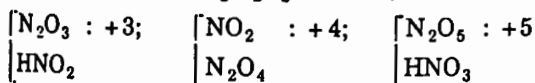
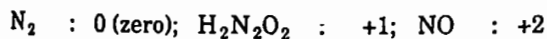
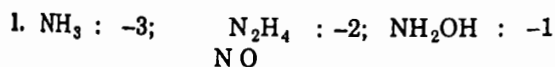


11.  $\text{NH}_3$  gas is dried by  $\text{CaO}$  and not by  $\text{P}_2\text{O}_5$  and  $\text{H}_2\text{SO}_4$ . Explain.

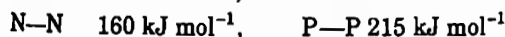
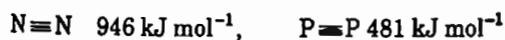
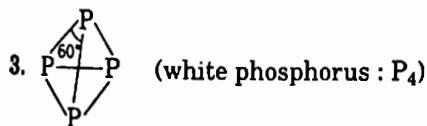
12. Identify (A), (B), (C) and (D) in the following:



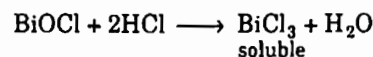
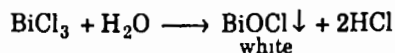
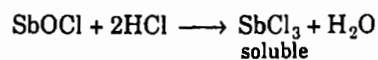
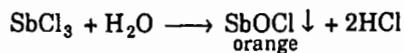
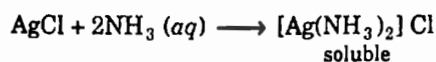
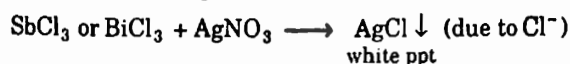
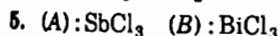
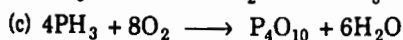
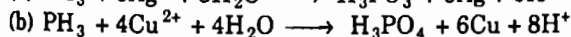
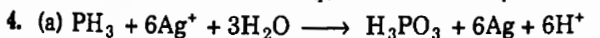
## Answers



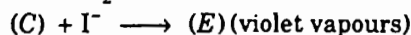
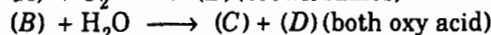
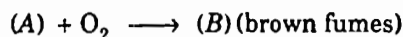
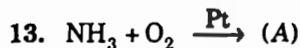
2. Nitrogen ( $1s^2 2s^2 2p^3$ ) lacks  $2d$ -orbitals in which electrons of  $2s$  can be excited to make five orbitals unpaired. Only three electrons remain unpaired hence only  $\text{NX}_3$  is formed. In case of  $\text{P}(1s^2 2s^2 2p^6 3s^2 3p^3)$ ,  $3s$  electron can be excited into  $3d$  vacant orbitals thus making five unpaired electrons, thus  $\text{PX}_5$  is possible.



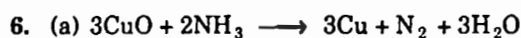
Greater the B.E., greater the stability [compare BE of  $\text{N} \equiv \text{N}$  and  $\text{P} \equiv \text{P}$  and  $\text{N}-\text{N}$  (in  $\text{N}_2$ ) and  $\text{P}-\text{P}$  (in  $\text{P}_4$ )]



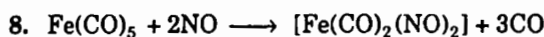
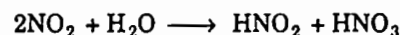
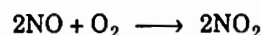
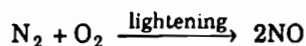
Turbidity can be dissolved in dil.  $\text{HCl}$ .



Identify (A), (B), (C), (D) and (E).

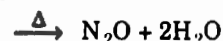
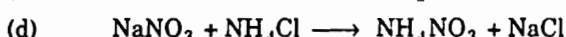
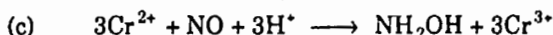
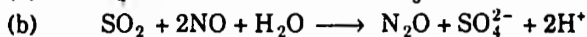
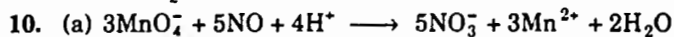
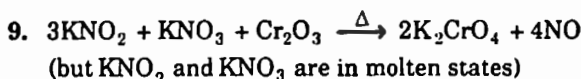


7. Lightning forms  $\text{NO}$  which is converted to  $\text{NO}_2$ ,  $\text{HNO}_2$  and  $\text{HNO}_3$  under atmospheric conditions. Thus,  $\text{NO}_3^-$  is a source of nutrients (fertilisers) to the plant. Thus, there are chances of better crops when lightning occurs.

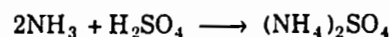
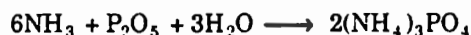


$\text{CO}$  donates two electrons while  $\text{NO}$  three electrons, hence electrons lost (due to  $\text{CO}$ ) = six

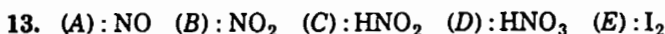
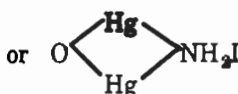
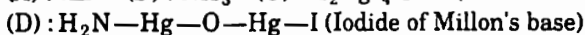
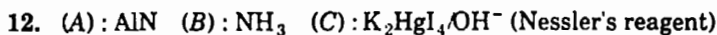
electrons gained (due to  $\text{NO}$ ) = six



11. Moist  $\text{NH}_3$  can react with  $\text{P}_2\text{O}_5$  forming phosphate and with conc.  $\text{H}_2\text{SO}_4$  forming sulphates :



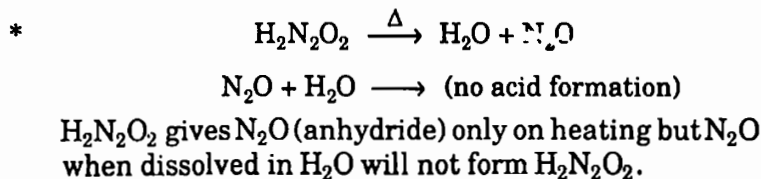
hence can't be used for drying  $\text{NH}_3$ .  $\text{CaO}$  being basic would only cause drying of  $\text{NH}_3$ .





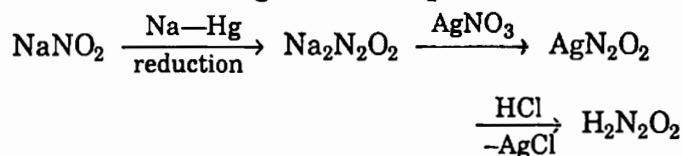
## Oxyacids of Nitrogen

| Acid             | Formula                          | Ox. no. | Anhydride              |
|------------------|----------------------------------|---------|------------------------|
| Hyponitrous acid | $\text{H}_2\text{N}_2\text{O}_2$ | +1      | $\text{N}_2\text{O}^*$ |
| Nitrous acid     | $\text{HNO}_2$                   | +3      | $\text{N}_2\text{O}_3$ |
| Nitric acid      | $\text{HNO}_3$                   | +5      | $\text{N}_2\text{O}_5$ |

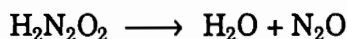


### Hyponitrous Acid ( $\text{H}_2\text{N}_2\text{O}_2$ )

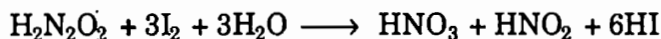
- It is obtained starting from  $\text{NaNO}_2$  :



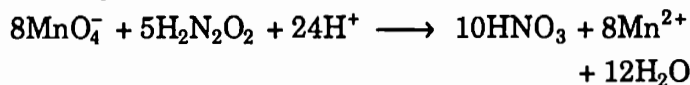
- Colourless leaflets hygroscopic crystals.
- In aqueous solution it decomposes :



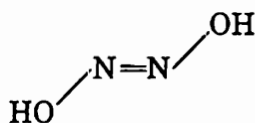
- Very weak dibasic acid but a strong reducing agent :  
 $\text{I}_2$  is reduced to  $\text{HI}$



- $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$

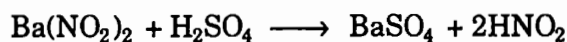


- It has zero dipole moment which is based on its *trans* structure :



### Nitrous Acid ( $\text{HNO}_2$ )

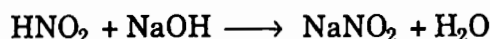
- Nitrous acid is unstable except in dilute solution. It is easily made by acidifying a solution of a nitrite :



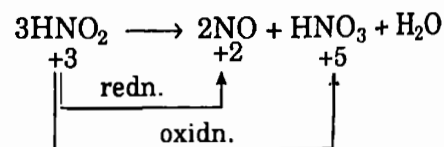
It appears as a pale blue solution (due to  $\text{N}_2\text{O}_3$ ) when nitrite is dissolved in acid. To prevent its decomposition, it must be kept below  $5^\circ\text{C}$ .

- $\text{N}_2\text{O}_3 + \text{H}_2\text{O} \longrightarrow 2\text{HNO}_2$
- $\text{NH}_3 + 3\text{H}_2\text{O}_2 \longrightarrow \text{HNO}_2 + 4\text{H}_2\text{O}$

- It is a weak acid ( $K_a = 4.5 \times 10^{-5}$ ) and



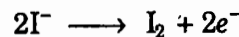
- It disproportionates to  $\text{HNO}_3$  (oxidation) and  $\text{NO}$  (reduction) even in cold solution



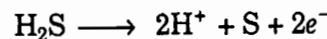
- As an oxidising agent :



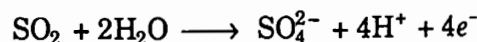
- it oxidises  $\text{I}^-$  to  $\text{I}_2$



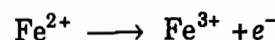
- it oxidises  $\text{H}_2\text{S}$  to  $\text{S}$



- it oxidises  $\text{SO}_2$  to  $\text{SO}_4^{2-}$



- it oxidises  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$

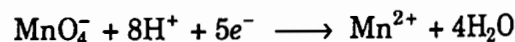


**Note :** Oxidation half-reaction may be added to reduction half reaction (I) to cancel electron in final reaction.

- As a reducing agent :

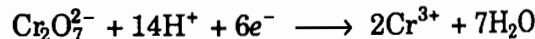


- It reduces acidified  $\text{MnO}_4^-$  (purple) to  $\text{Mn}^{2+}$  (colourless)

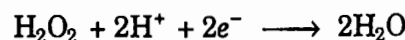


**Note :**  $\text{Mn}^{2+}$  salt are pink-coloured but appears colourless in aqueous solution.

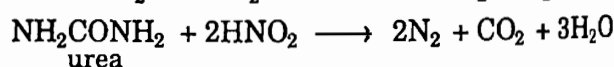
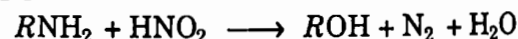
- it reduces acidified  $\text{Cr}_2\text{O}_7^{2-}$  (orange) to  $\text{Cr}^{3+}$  (green)



- it reduces  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{O}$

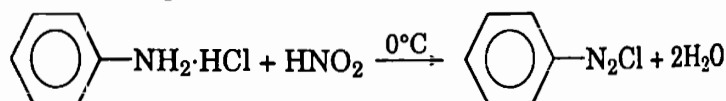


- Aliphatic amines and amides on reaction with  $\text{HNO}_2$  give  $\text{N}_2$  gas

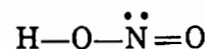


This provides the basis of Duma's method of estimation of nitrogen quantitatively in organic compounds.

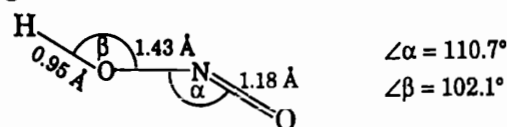
- However, aromatic amines form diazonium salts at low temperature (diazotisation)



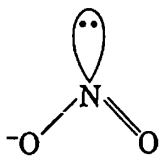
- It behaves as a monobasic acid and has structure



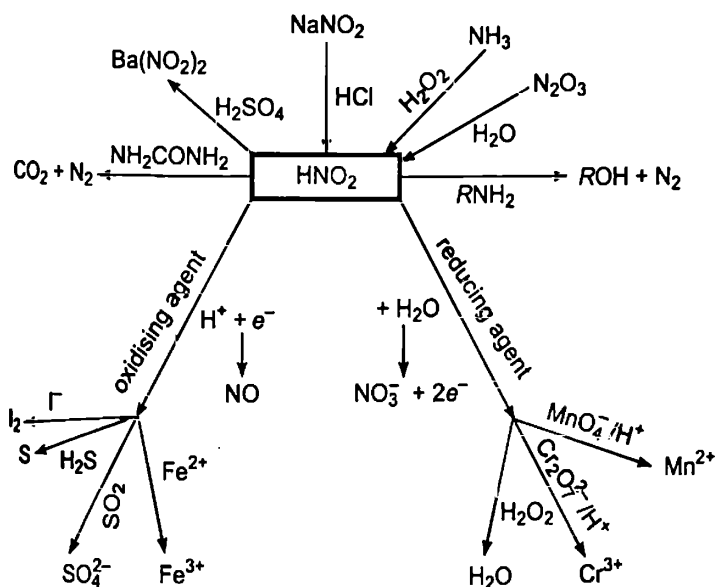
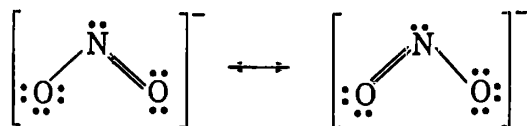
Microwave spectroscopic studies have shown that nitrous acid in the gaseous state has *trans* configuration :



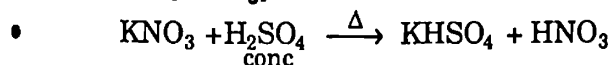
$\text{NO}_2^-$  has planar triangular structure, with N at the centre, two corners occupied by O atoms, and the third corner occupied by the lone pair.



Nitrite ion can exist in the following resonance structures :

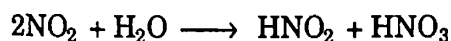
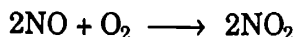
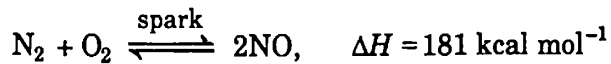


## Nitric Acid ( $\text{HNO}_3$ )

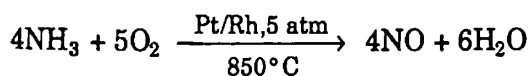


On condensation, vapours of  $\text{HNO}_3$  changes to liquid state (a laboratory method).

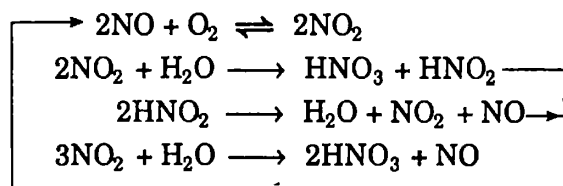
- Birkeland-Eyde process** involves electric sparking of  $\text{N}_2$  and  $\text{O}_2$  and passing of the gas into  $\text{H}_2\text{O}$ .



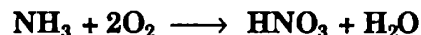
- Ostwald process** depends on the catalytic oxidation of  $\text{NH}_3$  to  $\text{NO}$ , followed by oxidation of  $\text{NO}$  to  $\text{NO}_2$ , and conversion of  $\text{NO}_2$  with  $\text{H}_2\text{O}$  to  $\text{HNO}_3$ .



The  $\text{NO}$  and air are cooled and the mixture of gases is absorbed in a counter current of water.

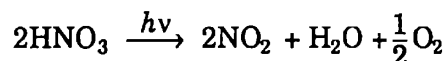


Overall reaction being



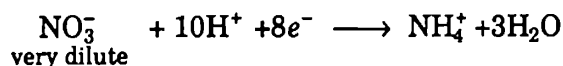
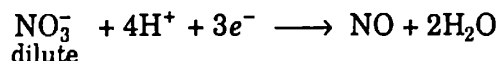
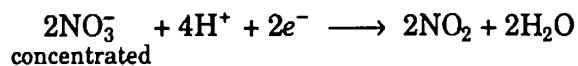
Acid is 60% by weight and concentrated  $\text{HNO}_3$  (98% by weight) is obtained by dehydration with conc.  $\text{H}_2\text{SO}_4$ . Fuming  $\text{HNO}_3$  contains dissolved  $\text{NO}_2$  in concentrated nitric acid.

- Anhydrous  $\text{HNO}_3$  is colourless fuming and pungent smelling liquid, soluble in water; boiling point =  $84.1^\circ\text{C}$  and freezing point =  $41.55^\circ\text{C}$ . On account of photochemical decomposition (in sunlight), it is often of yellow colour.

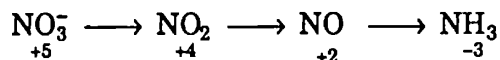


- Its auto-ionisation gives  $\text{NO}_2^+$  (nitronium ion) and  $\text{NO}_3^-$   

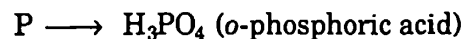
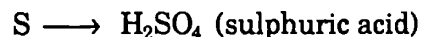
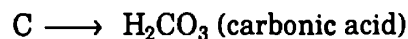
$$2\text{HNO}_3 \longrightarrow \text{NO}_2^+ + \text{NO}_3^- + \text{H}_2\text{O}$$
- It is a strong monobasic acid and forms nitrates with carbonates, oxides and hydroxides.
- $\text{HNO}_3$  is a powerful oxidising agent :



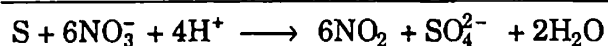
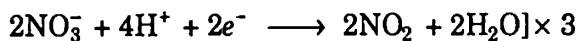
Thus oxidising power of  $\text{HNO}_3$  depends on the extent of dilution.



- Non-metals are oxidised to their oxyacids by conc.  $\text{HNO}_3$ .



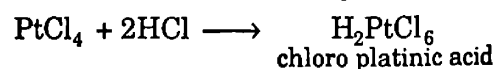
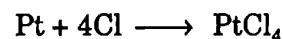
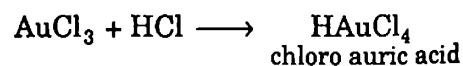
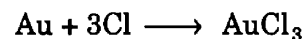
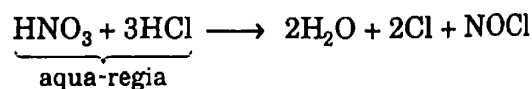
One reaction is given to explain, others may be written similarly.



Metals are oxidised forming nitrates and  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$  or  $\text{NH}_3$  depending on the nature of the metal, the temperature and the concentration of the acid. Reactions of metals with  $\text{HNO}_3$  are summarised in Table 13.3.

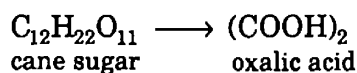
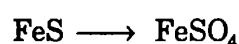
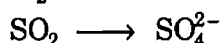
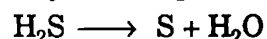
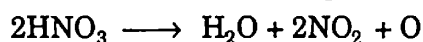
**DEEP Focus**

- Noble metals like Au, Pt, Rh and Ir are not attacked by nitric acid. Aqua regia, which is a mixture of 75% conc HCl and 25% conc.  $\text{HNO}_3$  can dissolve Au and Pt. The enhanced ability to dissolve metals shown by aqua-regia arises from the oxidising power of  $\text{HNO}_3$  coupled with the ability of  $\text{Cl}^-$  to form complexes with the metal ions.

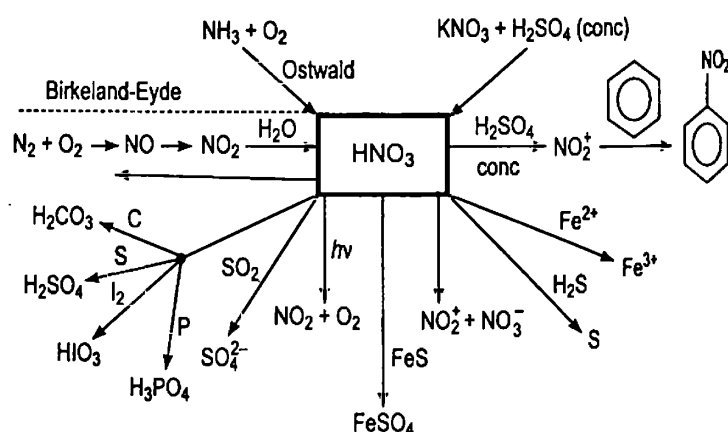
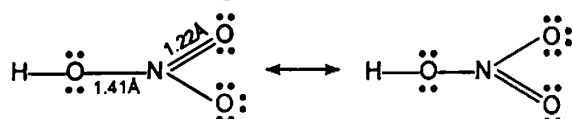
**Table 13.3 Reactions of Elements (Metals/Metalloids with  $\text{HNO}_3$ )**

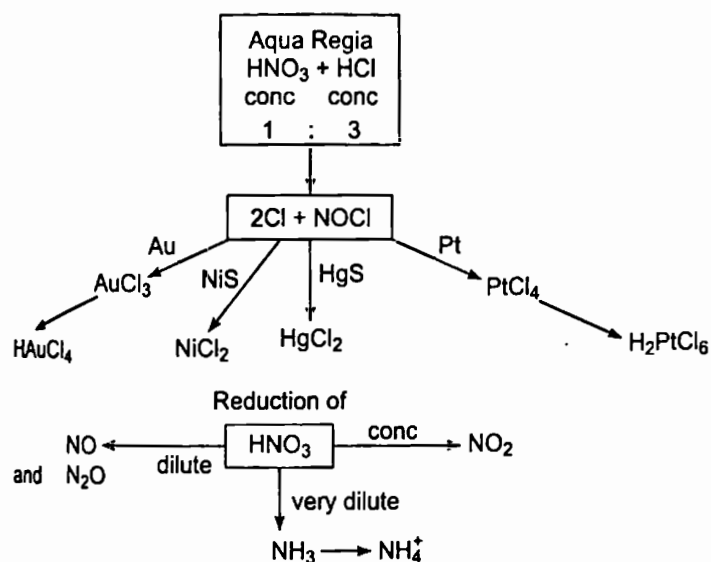
| Element                                                   | Nature of $\text{HNO}_3$ | $\text{HNO}_3$ changes to | Reactions                                                                                                                                               |
|-----------------------------------------------------------|--------------------------|---------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------|
| (A) Metals placed above H in electrochemical series (ECS) |                          |                           |                                                                                                                                                         |
| 1. Mg, Mn                                                 | dilute                   | $\text{M}(\text{NO}_3)_2$ | $\text{M} + 2\text{HNO}_3 \longrightarrow \text{M}(\text{NO}_3)_2 + \text{H}_2$                                                                         |
| 2. Zn, Fe                                                 | (a) very dilute          | $\text{NH}_4\text{NO}_3$  | $4\text{Zn} + 10\text{HNO}_3 \longrightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$                                  |
|                                                           | (b) dilute               | $\text{N}_2\text{O}$      | $4\text{Zn} + 10\text{HNO}_3 \longrightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}$                                      |
|                                                           | (c) conc                 | $\text{NO}_2$             | $\text{Zn} + 4\text{HNO}_3 \longrightarrow \text{Zn}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$<br>Fe becomes passive with 80% $\text{HNO}_3$ |
| 3. Sn                                                     | (a) dilute               | $\text{NH}_4\text{NO}_3$  | Refer 2(a).                                                                                                                                             |
|                                                           | (b) conc                 | $\text{NO}_2$             | $\text{Sn} + 4\text{HNO}_3 \longrightarrow \text{H}_2\text{SnO}_3 + 4\text{NO}_2 + \text{H}_2\text{O}$<br>meta stannic acid                             |
| 4. Pb                                                     | (a) dilute               | $\text{NO}$               | $3\text{Pb} + 8\text{HNO}_3 \longrightarrow 3\text{Pb}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$                                               |
|                                                           | (b) conc                 | $\text{NO}_2$             | Refer 2(c).                                                                                                                                             |
| (B) Metals below H in ECS                                 |                          |                           |                                                                                                                                                         |
| 5. Cu, Ag                                                 | (a) dilute               | $\text{NO}$               | Refer 4(a). Hg forms $\text{Hg}_2(\text{NO}_3)_2$                                                                                                       |
| Hg                                                        | (b) conc                 | $\text{NO}_2$             | Refer 4(c).                                                                                                                                             |
| (C) Metalloids                                            |                          |                           |                                                                                                                                                         |
| Sb, As                                                    | conc                     | $\text{NO}_2$             | $\text{Sb} + 5\text{HNO}_3 \longrightarrow \text{H}_3\text{SbO}_4 + 5\text{NO}_2 + \text{H}_2\text{O}$<br>antimonic acid                                |

- $\text{HNO}_3$  can also be used to oxidise compounds :



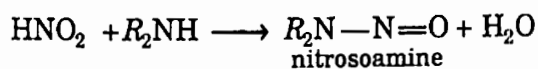
- Structure can be represented as:





### NaNO<sub>2</sub> and NaNO<sub>3</sub> as Food Additives

The brown colour of "old" meat is the result of oxidation of blood and is objectionable to many consumers. Nitrites and nitrates are added to food to retard this oxidation and also to prevent growth of botulism bacteria. NO<sub>3</sub><sup>-</sup> ions are reduced to NO<sub>2</sub><sup>-</sup> ions, which are then converted to NO. This in turn reacts with the brown oxidised form of the heme in blood. This reaction keeps meat red longer. However, there are doubts that nitrites may combine with amines under the acidic conditions in the stomach to give carcinogenic nitrosoamines.



## Study of Phosphorus and its Compounds

### Isolation of Phosphorus

Phosphorus is the most abundant element of group 15(VA), accounting for 0.1% of the mass of the earth's crust. Phosphorus is also important in living systems and is the **sixth** most abundant element in the human body. Our bones are mostly Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, and tooth enamel is almost pure Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH. Phosphate groups are an integral part of the nucleic acid DNA and RNA, the molecules that pass genetic information from generation to generation.

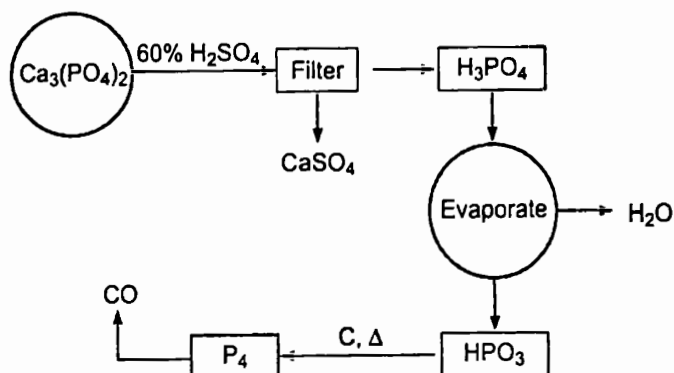
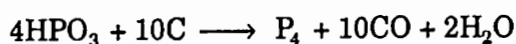
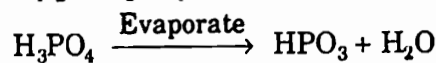
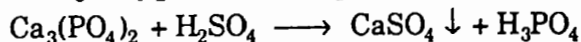
### Minerals

|                     |   |                                                                                                                             |
|---------------------|---|-----------------------------------------------------------------------------------------------------------------------------|
| Phosphorite         | : | Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>                                                                             |
| Fluorapatite        | : | 3Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> · CaF <sub>2</sub><br>or Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F |
| Chlorapatite        | : | 3Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> · CaCl <sub>2</sub>                                                        |
| Aluminium phosphate | : | AlPO <sub>4</sub>                                                                                                           |
| Ferric phosphate    | : | FePO <sub>4</sub>                                                                                                           |

Phosphorus exists in three common **allotropic** forms

- (i) white phosphorus
- (ii) red phosphorus
- (iii) black phosphorus

(i) **White phosphorus** In earlier days, white phosphorus was obtained by the distillation of metaphosphoric acid (HPO<sub>3</sub>) with carbon at high temperature. HPO<sub>3</sub>, in turn was obtained by decomposing bone-ash [Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>] with 60% H<sub>2</sub>SO<sub>4</sub>.



In modern electrochemical process, white phosphorus is manufactured by heating a mixture of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, sand and coke at 1500°C in a furnace by means of an electric arc (Fig. 13.3). The reactions are:

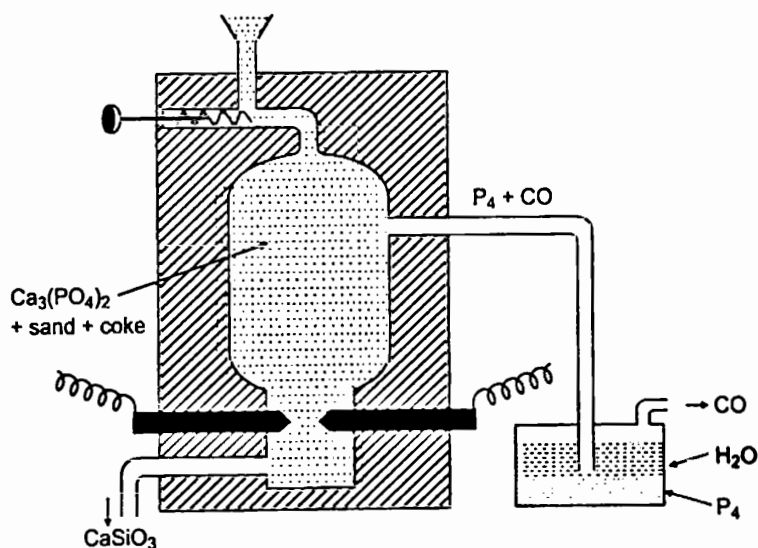
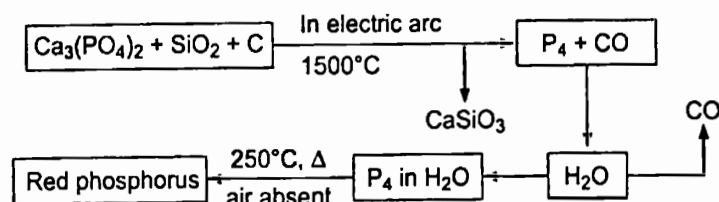
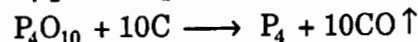
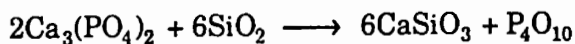


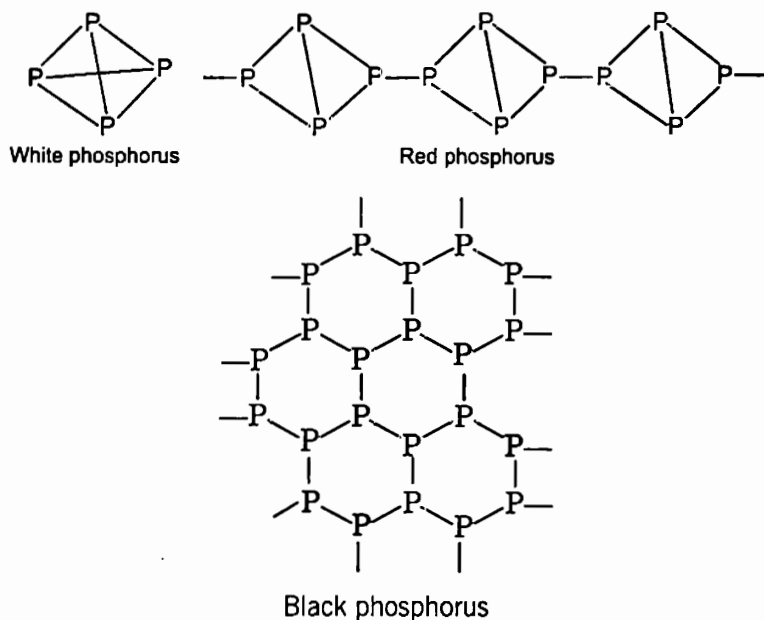
Fig. 13.3 Manufacture of phosphorus by electrochemical process

The calcium silicate forms a slag and is run off through an outlet at the bottom of the furnace. Phosphorus vapor issues through an opening at the top of the furnace is condensed under water.

**(ii) Red phosphorus** Red phosphorus is prepared by heating white phosphorus in the absence of air at  $250^{\circ}\text{C}$  for a few hours with a trace of iodine as catalyst in a closed iron vessel fitted with a safety valve. At the end of conversion, the product is ground under water and treated with hot caustic soda solution to eliminate any unchanged white phosphorus. It is finally washed with hot water and dried by heating with steam.

**(iii) Black phosphorus** It is obtained by heating white phosphorus at 470 K under high pressure. A series of phases of black phosphorus are formed and one of these phases consists of an extended layer structure in which each phosphorus is bonded to three neighbours by single covalent bonds. Thermodynamically, black phosphorus is the most stable form.

White phosphorus, the form produced in the industrial synthesis, is a toxic, waxy, white solid that contains discrete tetrahedral  $\text{P}_4$  molecules. Red phosphorus, by contrast, is essentially nontoxic and has a polymeric structure:



As expected for a molecular solid that contains small, non-polar molecules, white phosphorus has a low melting point ( $44^{\circ}\text{C}$ ) and is soluble in non-polar solvents such as  $\text{CS}_2$ . It is highly reactive, bursting into flames when exposed to air, and is thus **stored under water**.

Consistent with its polymeric structure, red phosphorus is higher melting (m.p.  $\sim 600^{\circ}\text{C}$ ), less soluble, less reactive than white phosphorus, and it does not ignite on contact with air. Comparative properties of white red and black phosphorus have been summarised, in Table 13.4.

Table 13.4 Comparison of White, Red and Black Phosphorus

| Properties                                  | White phosphorus           | Red phosphorus          | Black phosphorus |
|---------------------------------------------|----------------------------|-------------------------|------------------|
| 1. Colour                                   | White                      | Reddish-violet          | Black            |
| 2. Smell                                    | Garlic-like                | Odourless               | Odourless        |
| 3. Specific gravity                         | 1.83–1.85                  | 2.06–2.39               | $\approx 3.9$    |
| 4. Solubility in $\text{CS}_2$              | Soluble                    | Insoluble               | Insoluble        |
| 5. m.p./ $^{\circ}\text{C}$                 | 44                         | $\sim 600$              | $\sim 610$       |
| 6. Ignition temperature/ $^{\circ}\text{C}$ | 30                         | 260                     | $\sim$ Stable    |
| 7. Action of air                            | Phosphorescence            | No phosphorescence      | No               |
| 8. With $\text{Cl}_2$                       | Reacts at room temperature | Reacts only when heated | At m.p.          |
| 9. With NaOH                                | $\text{PH}_3$ is formed    | No reaction             | No reaction      |
| 10. Physiological effect                    | Poisonous                  | Non-poisonous           | Non-poisonous    |

**Illustration 1** Explain the high reactivity of white phosphorus.

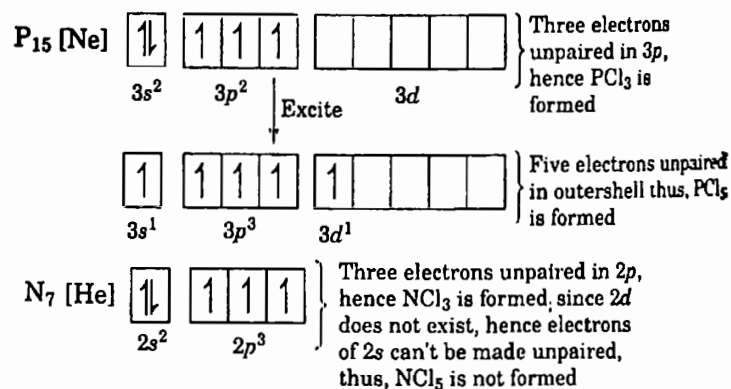
**Solution** The high reactivity of white phosphorus is due to an unusual bonding that produces considerable strain in the  $\text{P}_4$  molecules. If each P atom uses  $3p$  orbitals to form three P–P bonds, all the bond angles should be  $90^{\circ}$ . The geometry of  $\text{P}_4$ , however, requires that all the bonds have  $60^{\circ}$  angles, which means that the  $p$ -orbitals cannot overlap in a head-on-fashion. As a result, the P–P bonds are “bent”, relatively weak, and highly reactive.

**Note:** White phosphorus was once used in matches, but because of its toxicity it has been replaced by  $\text{P}_4\text{S}_3$ .

## Compounds of Phosphorus

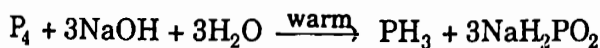
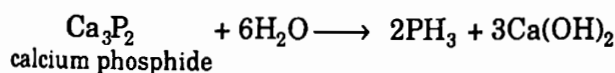
### DEEP Focus

- Phosphorus and the other members of the group can make use of  $d$ -orbitals in their bonding, and thus +5 oxidation state is shown beside +3 which is common in all the compounds. Thus,  $\text{PCl}_5$  is formed while  $\text{NCl}_5$  is not formed.

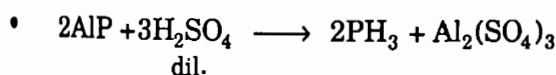
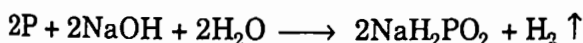


## Phosphine (PH<sub>3</sub>)

- Phosphine can be formed by :



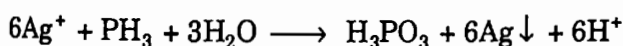
It is necessary to exclude air from the apparatus because, although pure PH<sub>3</sub> will not burn unless ignited, it is often accompanied with P<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> which are spontaneously flammable.



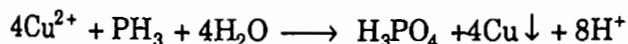
- It is a colourless, highly reactive and extremely toxic gas, which smells slightly of garlic or bad fish.

- It is better reducing agent than NH<sub>3</sub>

- Ag<sup>+</sup> is reduced to Ag metal



- Cu<sup>2+</sup> is reduced to Cu

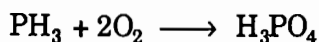


- PH<sub>3</sub>, unlike NH<sub>3</sub>, is not very soluble in water. Its aqueous solution is neutral.

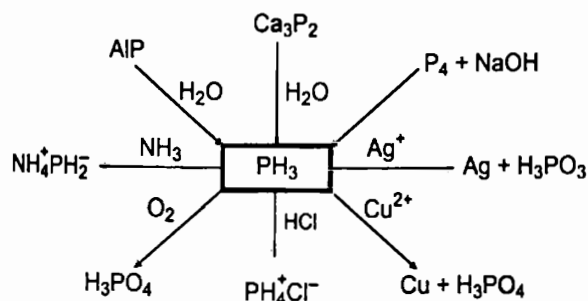
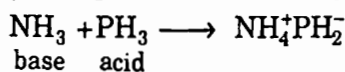
- It is more soluble in CS<sub>2</sub> and other organic solvents.

- Anhydrous PH<sub>3</sub> and anhydrous HCl (not in aqueous solution) combine to form PH<sub>4</sub><sup>+</sup>Cl<sup>-</sup>

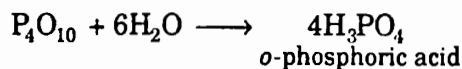
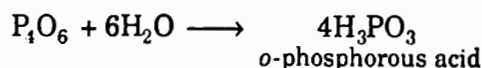
- Pure PH<sub>3</sub> is stable in air, but it catches fire when heated to about 150°C.



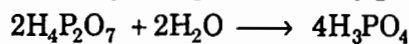
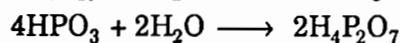
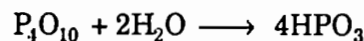
- In liquid NH<sub>3</sub>, phosphine dissolves to give NH<sub>4</sub><sup>+</sup>PH<sub>2</sub><sup>-</sup>



The oxides of phosphorus react vigorously with H<sub>2</sub>O to give acidic solution :

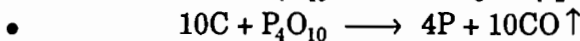
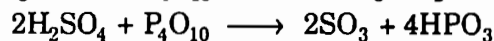
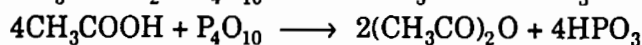
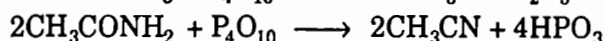
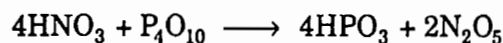


This takes place in stages :

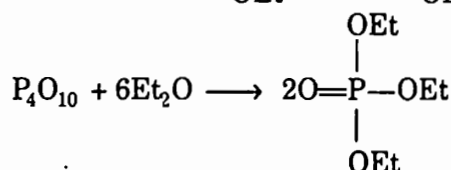
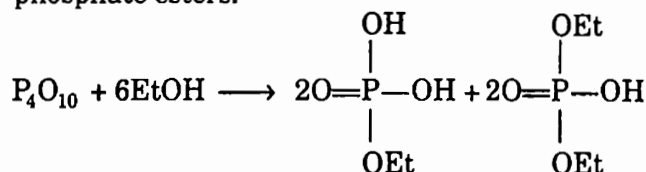


## DEEP Focus

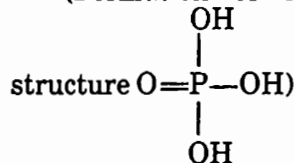
- P<sub>4</sub>O<sub>10</sub> is a white flocculent powder that has greater affinity for water hence, is used as dehydrating agent in:



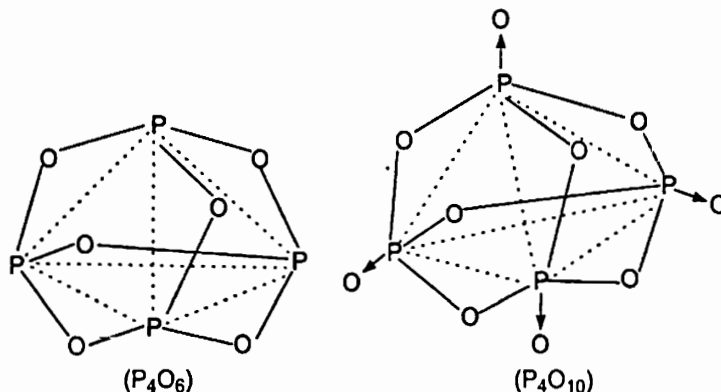
- P<sub>4</sub>O<sub>10</sub> reacts with alcohols and ethers forming phosphate esters:



(Formation of esters confirms that H<sub>3</sub>PO<sub>4</sub> has



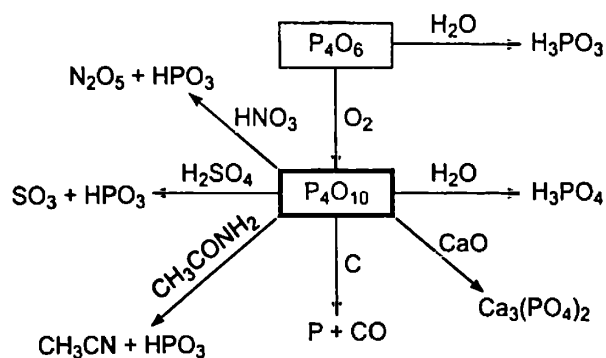
- The basic building block of both of them is a tetrahedron of P-atoms. In P<sub>4</sub>O<sub>6</sub>, oxygen atoms act as a bridge between the corners of the tetrahedron. In P<sub>4</sub>O<sub>10</sub>, each P-atom is also bonded to an extra oxygen atom. Each oxide (P<sub>4</sub>O<sub>6</sub>, P<sub>4</sub>O<sub>10</sub>) has six POP bonds.



## Oxides of Phosphorus

Two important oxides of phosphorus are known :

| Oxides                         | Oxoacids                       | Oxidation number |
|--------------------------------|--------------------------------|------------------|
| P <sub>4</sub> O <sub>6</sub>  | H <sub>3</sub> PO <sub>3</sub> | +3               |
| P <sub>4</sub> O <sub>10</sub> | H <sub>3</sub> PO <sub>4</sub> | +5               |



## Oxoacids of Phosphorus

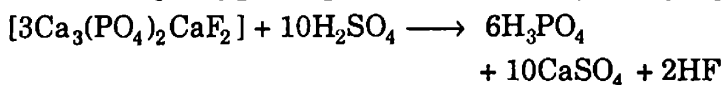
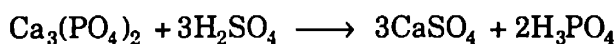
- Following oxoacids of phosphorus are commonly known :

Table 13.5

| Acid                                | Basicity | Name                                             | Oxidation no. |
|-------------------------------------|----------|--------------------------------------------------|---------------|
| $\text{H}_3\text{PO}_2$             | 1        | Phosphinic acid<br>(hypophosphorous acid)        | +1            |
| $\text{H}_3\text{PO}_3$             | 2        | Phosphonic acid<br>( $\alpha$ -phosphorous acid) | +3            |
| $\text{H}_3\text{PO}_4$             | 3        | Phosphoric acid<br>( $\alpha$ -phosphoric acid)  | +5            |
| $\text{HPO}_3$                      | 1        | Metaphosphoric acid                              | +5            |
| $\text{H}_4\text{P}_2\text{O}_7$    | 4        | Pyrophosphoric acid                              | +5            |
| $\text{H}_5\text{P}_3\text{O}_{10}$ | 5        | Triphosphoric acid                               | +5            |

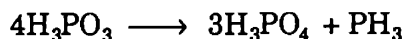
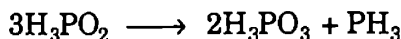
### Wet Process

- $\text{H}_3\text{PO}_4$  is obtained when phosphate rock reacts with  $\text{H}_2\text{SO}_4$ .



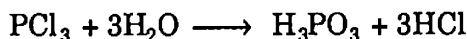
### Furnace Process

- $\text{P}_4 + 5\text{O}_2 \longrightarrow \text{P}_4\text{O}_{10}$   
 $\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \longrightarrow 4\text{H}_3\text{PO}_4$
- $\text{H}_3\text{PO}_2$  and  $\text{H}_3\text{PO}_3$  disproportionate to  $\text{PH}_3$  and  $\text{H}_3\text{PO}_4$  on heating :

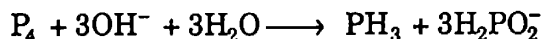


- $\text{P}_4 + 20\text{HNO}_3 \longrightarrow 4\text{H}_3\text{PO}_4 + 20\text{NO}_2 + 4\text{H}_2\text{O}$

- $\text{H}_3\text{PO}_3$  is formed by hydrolysis of  $\text{PCl}_3$ :



- $\text{H}_3\text{PO}_2$  is obtained by alkaline hydrolysis of  $\text{P}_4$ :

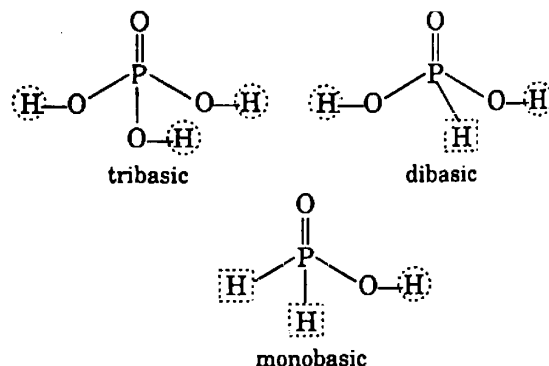


- Table 13.6 gives distinction between  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_2$ .

- Phosphoric acid,  $\text{H}_3\text{PO}_4$ , is hydrogen bonded in aqueous solution, and because of this the 'concentrated acid' is syrupy and viscous.

## DEEP Focus

- In all of these acids, P is four-coordinate and tetrahedrally surrounded wherever possible  $p\pi - p\pi$  back bonding gives rise to  $\text{P}=\text{O}$  bonds. The hydrogen atoms in  $\text{O}-\text{H}$  groups are ionisable and are acidic, but  $\text{P}-\text{H}$  bonds found in phosphorous acids have reducing and not the acidic properties.
- Also basicity = number of ionisable H (protonic) = H attached to O-atoms  
(H encircled are acidic and H squared indicates reducing properties)



- Thus :

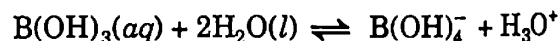
- all P atoms in the oxoacids and oxoanions (conjugate base) are 4-coordinate and contain at least one  $\text{P}-\text{O}$  unit,
- all P atoms in the oxoacids have at least one  $\text{P}-\text{OH}$  group. In every case, the H atom is ionisable as  $\text{H}^+$ .
- some oxoacids have one or more  $\text{P}-\text{H}$  bonds. This H atom is not ionisable as  $\text{H}^+$ .
- Polymerisation can occur by  $\text{P}-\text{O}-\text{P}$  bond formation to give both linear and cyclic species. Two P atoms are never joined by more than one  $\text{P}-\text{O}-\text{P}$  bridge.
- When P atom is surrounded by O atoms (as in  $\text{H}_3\text{PO}_4$ ) its oxidation number is +5. For each  $\text{P}-\text{OH}$  that is replaced by  $\text{P}-\text{H}$  bond, its oxidation number drops by 2.

**Illustration 2** Write balanced equations for the reactions of  $\text{H}_3\text{PO}_4$  and  $\text{B}(\text{OH})_3$  with water. Classify each acid as Bronsted-Lowry acid or a Lewis acid.

### Solution



Since,  $\text{H}_3\text{PO}_4$  is proton-donor hence,  $\text{H}_3\text{PO}_4$  is a Bronsted-Lowry acid and  $\text{H}_2\text{O}$  which is a proton-acceptor is a Bronsted-Lowry base.



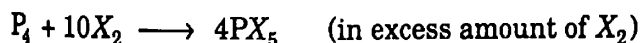
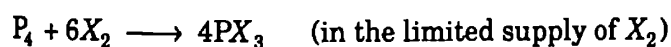
$\text{B}(\text{OH})_3$  has electron-deficient B (octet incomplete) hence, it accepts electron-pair from  $\text{H}_2\text{O}$ . Thus,  $\text{B}(\text{OH})_3$  is a Lewis acid.

Table 13.6 Distinctive Properties of Oxoacids of Phosphorus

| Properties             | H <sub>3</sub> PO <sub>2</sub>                                                                                                                                                                                                                                                                                                       | H <sub>3</sub> PO <sub>3</sub>                                                                                                                                                                                                                                                                                                                                                                                        | H <sub>3</sub> PO <sub>4</sub>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
|------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1. Basicity            | Monobasic<br>H <sub>3</sub> PO <sub>2</sub> ⇌ H <sup>+</sup> + H <sub>2</sub> PO <sub>2</sub> <sup>-</sup> hence only one type of salt (like NaH <sub>2</sub> PO <sub>2</sub> ) is formed.<br>NaH <sub>2</sub> PO <sub>2</sub> is normal salt (which does not further react with base or which is without protonic H <sup>+</sup> ). | Dibasic<br>H <sub>3</sub> PO <sub>3</sub> ⇌ H <sup>+</sup> + H <sub>2</sub> PO <sub>3</sub> <sup>-</sup><br>H <sub>2</sub> PO <sub>3</sub> <sup>-</sup> ⇌ H <sup>+</sup> + HPO <sub>3</sub> <sup>2-</sup> Two types of salts, NaH <sub>2</sub> PO <sub>3</sub> and Na <sub>2</sub> HPO <sub>3</sub> are formed. NaH <sub>2</sub> PO <sub>3</sub> is an acid salt but Na <sub>2</sub> HPO <sub>3</sub> is normal salt. | Tribasic<br>H <sub>3</sub> PO <sub>4</sub> ⇌ H <sup>+</sup> + H <sub>2</sub> PO <sub>4</sub> <sup>-</sup><br>H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> ⇌ H <sup>+</sup> + HPO <sub>4</sub> <sup>2-</sup><br>HPO <sub>4</sub> <sup>2-</sup> ⇌ H <sup>+</sup> + PO <sub>4</sub> <sup>3-</sup> Three series of salts, NaH <sub>2</sub> PO <sub>4</sub> , Na <sub>2</sub> HPO <sub>4</sub> and Na <sub>3</sub> PO <sub>4</sub> are formed. NaH <sub>2</sub> PO <sub>4</sub> and Na <sub>2</sub> HPO <sub>4</sub> are acid salts but Na <sub>3</sub> PO <sub>4</sub> is normal salt. |
| 2. Effect of heat      | 2H <sub>3</sub> PO <sub>2</sub> $\xrightarrow{\Delta}$ H <sub>3</sub> PO <sub>4</sub> + PH <sub>3</sub><br>disproportionation                                                                                                                                                                                                        | 4H <sub>3</sub> PO <sub>3</sub> $\xrightarrow[200^{\circ}\text{C}]{\Delta}$ 3H <sub>3</sub> PO <sub>4</sub> + PH <sub>3</sub><br>disproportionation                                                                                                                                                                                                                                                                   | H <sub>3</sub> PO <sub>4</sub> $\xrightarrow[600^{\circ}\text{C}]{\Delta}$ HPO <sub>3</sub> + H <sub>2</sub> O<br>dehydration                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
| 3. Reducing properties | Most reducing agent<br>AgNO <sub>3</sub> → Ag<br>HgCl <sub>2</sub> → Hg<br>CuSO <sub>4</sub> → Cu <sub>2</sub> H <sub>2</sub><br>Cl <sub>2</sub> → HCl                                                                                                                                                                               | AgNO <sub>3</sub> → Ag<br>HgCl <sub>2</sub> → Hg <sub>2</sub> Cl <sub>2</sub><br>CuSO <sub>4</sub> → Cu<br>MnO <sub>4</sub> <sup>-</sup> → Mn <sup>2+</sup>                                                                                                                                                                                                                                                           | Does not reduce salts into metals.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |

## Phosphorus Halides

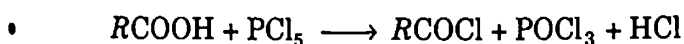
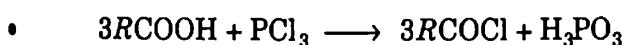
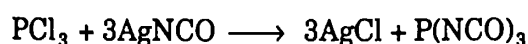
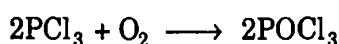
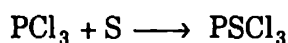
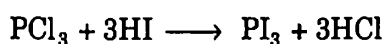
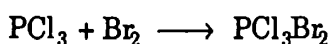
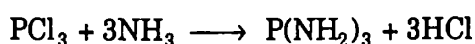
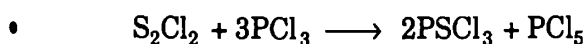
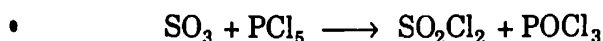
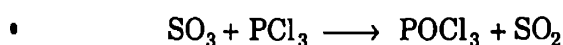
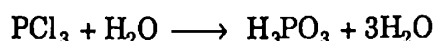
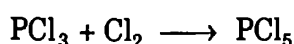
Two series of halides are known PX<sub>3</sub> and PX<sub>5</sub>, where X = halogen. Among these PI<sub>5</sub> is doubtful, whereas iodine forms a stable di-iodide P<sub>2</sub>I<sub>4</sub>.



All these halides are gases, volatile liquids or low-melting solids.

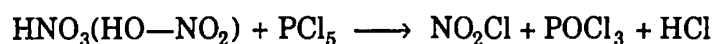
- PCl<sub>3</sub> is a colourless liquid (sp. grav. = 1.6, b.p. = 76°C).
- PCl<sub>5</sub> is an off-white solid m.p. = 167°C).

It fumes strongly in moist air and reacts strongly with H<sub>2</sub>O giving phosphorous acid.

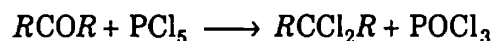
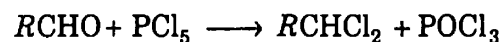


- $3\text{ROH} + \text{PCl}_3 \longrightarrow 3\text{RCl} + \text{H}_3\text{PO}_3$
- $\text{ROH} + \text{PCl}_5 \longrightarrow \text{RCl} + \text{POCl}_3 + \text{HCl}$
- $\text{SO}_2(\text{OH})_2 + \text{PCl}_5 \longrightarrow \text{SO}_2\text{Cl}_2 + 2\text{POCl}_3 + 2\text{HCl}$

In all the oxo-acids and hydroxy compounds, —OH group is replaced by Cl.

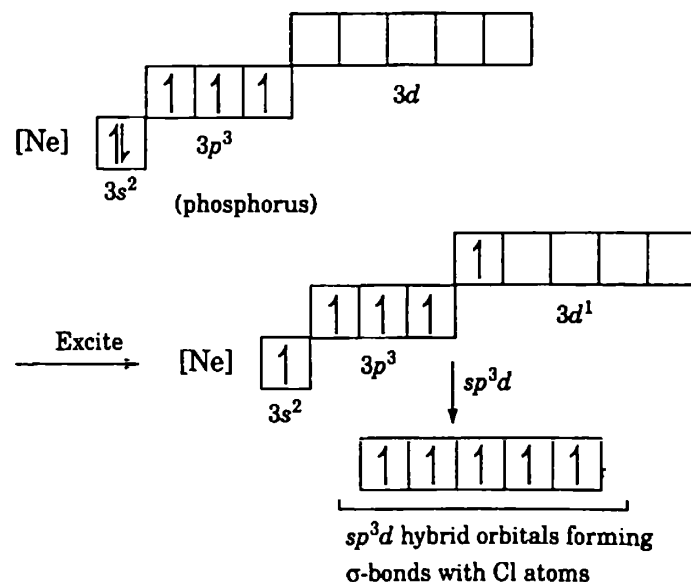


- In carbonyl compounds, O is replaced by two Cl atoms.



POCl<sub>3</sub> is the chloroanhydride of phosphoric acid.

- In the liquid and vapour states, PCl<sub>5</sub> has the trigonal bipyramidal structure, P atom being sp<sup>3</sup>d-hybridised.





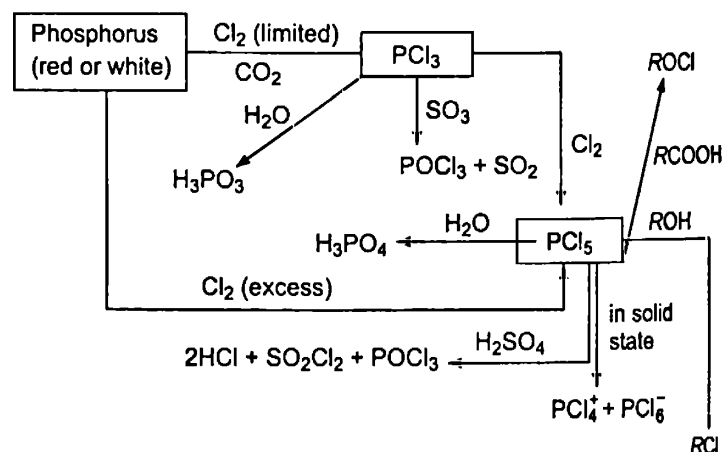
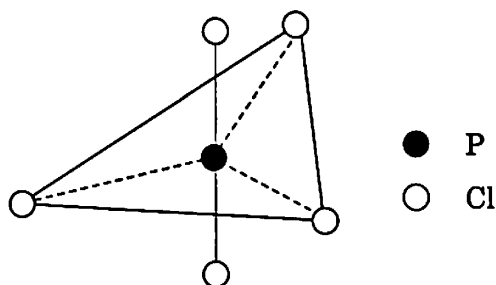


Table 13.7 Comparison between Nitrogen and Phosphorus

| Properties                | Nitrogen                                                                                                                                                                                                                                            | Phosphorus                                                                                                                                                                                                                                                                               |
|---------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1. Physical state         | N <sub>2</sub> is a gas which can be condensed to a liquid at very low temperature.                                                                                                                                                                 | P <sub>4</sub> is a solid at room temperature.                                                                                                                                                                                                                                           |
| 2. Bond energy            | N≡N (multiple bonds) are present in N <sub>2</sub><br>N≡N B.E. : 941.4 kJ mol <sup>-1</sup><br>Due to high value of bond energy (N≡N), it is less reactive and more stable<br>$\text{N}_2 + \text{O}_2 \xrightarrow{3300^\circ\text{C}} 2\text{NO}$ | Multiple bonds are absent in P<br>P—P B.E. : 79.08 kJ mol <sup>-1</sup><br>Due to low value of (P—P) bond energy P <sub>4</sub> is less stable and more reactive<br>$\text{P}_4 + 5\text{O}_2 \longrightarrow \text{P}_4\text{O}_{10}$<br>This reaction takes place at room temperature. |
| 3. Formation of compounds | NCl <sub>3</sub> is formed but NCl <sub>5</sub> is not formed since N cannot expand its octet due to lack of d-orbital.                                                                                                                             | Both PCl <sub>3</sub> and PCl <sub>5</sub> are formed due to expansion of octet.                                                                                                                                                                                                         |
| 4. Hydride                | NH <sub>3</sub> is more stable than PH <sub>3</sub> .<br>NH <sub>3</sub> is highly soluble in water due to H-bonding with water, giving alkaline solution.                                                                                          | Also PH <sub>4</sub> <sup>+</sup> is less stable than NH <sub>4</sub> <sup>+</sup> .<br>PH <sub>3</sub> is sparingly soluble in water and the solution is neutral-the hydrogen bond in latter is very weak.                                                                              |
| 5. Oxyacids               | Oxyacids of nitrogen are stronger than those of phosphorus.<br>HNO <sub>3</sub> is a strong oxidising agent.                                                                                                                                        | H <sub>3</sub> PO <sub>4</sub> is weaker acid than HNO <sub>3</sub> .<br>H <sub>3</sub> PO <sub>4</sub> is not oxidising agent.                                                                                                                                                          |

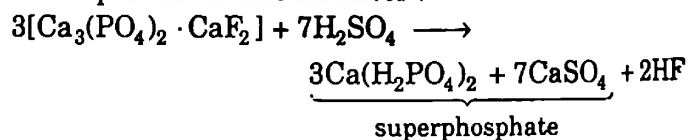
## Fertilizers

- Nitrogen, phosphorus and potassium are three most essential plant nutrients consumed by them. Fertility of soil is maintained by using these nutrients in the form of fertilizers.
- Fertilizer used should :  
be water soluble.  
not disturb alkaline nature (pH).  
be stable.
- NH<sub>2</sub>CONH<sub>2</sub> (urea)  
NH<sub>4</sub>NO<sub>3</sub> (ammonium nitrate)  
(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (ammonium sulphate)  
NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (mono ammonium hydrogen phosphate)

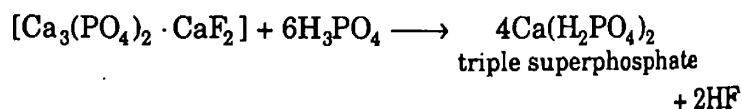
These are either used on their own or in conjugation with other chemicals, often to make **NPK** fertilisers. These are designed to release nitrogen (N), phosphorus (P) and potassium (K) into the soil. If the NPK fertiliser is marked 4-8-2, it means it has :

|    |                               |
|----|-------------------------------|
| 4% | N <sub>2</sub>                |
| 8% | P <sub>2</sub> O <sub>5</sub> |
| 2% | K <sub>2</sub> O              |

- Phosphate rocks such as fluoroapatite (Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> · CaF<sub>2</sub>) are very insoluble, and thus are not used as fertilisers. **Superphosphate** is made by treating phosphate rock with conc. H<sub>2</sub>SO<sub>4</sub>. The acid salt Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> is more soluble, and over a period of weeks this would dissolve in the soil water. CaSO<sub>4</sub> is waste product of this fertiliser :



- 'Triple superphosphate' is made using H<sub>3</sub>PO<sub>4</sub> and thus waste product CaSO<sub>4</sub> is not formed.



## Uses

A major use of phosphoric acid is to impart corrosion resistance to metal objects such as nuts, bolts, tools and car engine parts by plunging the object into hot acid bath. Car bodies are similarly treated with phosphoric acid

containing metal ions such as  $\text{Zn}^{2+}$ , and aluminium trim is "polished" by treating it with acid.

Red phosphorus is used in matches, fire works and as a component of phosphor-bronze alloys used for making bearings. The main use of elemental arsenic, antimony and bismuth is in the production of various alloys.

Besides the use of elemental nitrogen, compounds of nitrogen have extensive applications in various fields. Ammonia is used in various forms as a fertiliser, e.g., as  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{HPO}_4$ , etc. Its applications also include refrigeration, as a pH controller in food and beverage industry, pharmaceuticals and in water purification. Nitric acid is another important compound of nitrogen. Its major uses include manufacture of  $\text{NH}_4\text{NO}_3$ , explosives like nitroglycerine, nitrocellulose and TNT. Hydrazine,  $\text{N}_2\text{H}_4$  and its methyl derivatives,  $\text{MeNHNH}_2$  and  $\text{Me}_2\text{NNH}_2$ , are used as rocket fuels. Nitrous oxide,  $\text{N}_2\text{O}$ , is used as an anaesthetic.

Sulphides of phosphorus,  $\text{P}_4\text{S}_3$  and  $\text{P}_4\text{S}_{10}$  are used in match industry. Phosphoric acid is used as fertilisers, cleaning of metals, rust proofing, pharmaceuticals, etc.

Disodium hydrogen phosphate,  $\text{Na}_2\text{HPO}_4$ , is widely used as an emulsifier in the manufacture of pasteurised cheese. Sodium dihydrogen phosphate,  $\text{NaH}_2\text{PO}_4$ , is used as a constituent in the undercoat for metal paints. Calcium phosphates are used in baking powders and tooth-pastes. **Synthetic  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  (1-2%) is added to table salt to impart free flowing properties.** Sodium tripolyphosphate,  $\text{Na}_5\text{P}_3\text{O}_{10}$ , is used in detergents and in softening water. Phosphorus compounds like melathion, parathion, etc., are used as pesticides.

Arsenic compounds find extensive use in agriculture as herbicides for weed and pest control, e.g., monosodium methyl arsenate, MSMA and disodium methyl arsenate, DSMA. Arsenic acid is used as a wood preservative. Sodium arsenite is used for aquatic weed control. Arsenic oxide,  $\text{As}_2\text{O}_5$ , is used to decolourise bottle glass. Antimony compound, antimonial lead, is used in storage batteries. **Compounds of antimony with aluminium, gallium and indium,  $\text{AlSb}$ ,  $\text{GaSb}$  and  $\text{InSb}$ , find applications in infrared devices and in diodes.**

## Target Practice 2

- Nitrite ion ( $\text{NO}_2^-$ ) is said to interfere in the ring-test of nitrate ion ( $\text{NO}_3^-$ ). Name the chemical that can decompose  $\text{NO}_2^-$ .

.....

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  on reaction with  $\text{HNO}_2$  changes to 2-propanol as the main product. Explain the formation of 2-propanol.

.....

- Write the species of aqua-regia.

.....

What is the product when

(a) gold is dissolved in it? .....

(b) platinum is dissolved in it? .....

- Nitrites and nitrates are added to food to keep meat red for longer time. But there are harmful effects.

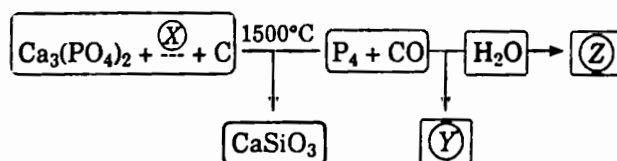
Harmful effects are .....

.....

- Anhydrous  $\text{HNO}_3$  is colourless but it is often yellow in colour due to .....

.....

- White phosphorus is manufactured by modern electrochemical process represented in the flow-sheet. Fill in the blank space X, Y and Z.



- Compare white and red phosphorus in the following properties.

|                                | White | Red   |
|--------------------------------|-------|-------|
| 1. Smell                       | ..... | ..... |
| 2. Solubility in $\text{CS}_2$ | ..... | ..... |
| 3. With NaOH                   | ..... | ..... |

- Write formula of phosgene and phosphine

.....

Of these

(a) Which is poisonous? .....

(b) Which is reducing agent .....

Write reactions of their formation.

**Phosgene**

**Phosphine**

- $\text{NH}_3$  is more basic than  $\text{PH}_3$ . It can be proved by .....

.....

- Many hundred years ago, a ship was transporting calcium carbide and calcium phosphide (stored in different container). By chance sea-water entered sea and luminous flame appeared. Passengers travelling in ship ran here to there assuming a ghost would have come. However, a chemist travelling in it explained it based on reactions. These reactions are .....

.....



## Practice Exercise 2

1.  $\text{HNO}_2$  can oxidise  $\text{I}^-$  to  $\text{I}_2$ ; suggest a suitable reagent that can estimate liberated  $\text{I}_2$ . Also determine equivalent weight of  $\text{HNO}_2$  in this estimation.
2.  $\text{Fe}^{2+}$  as well as  $\text{HNO}_2$  can be used to estimate  $\text{MnO}_4^-$  in acidic medium. If 100 mL of 1 M  $\text{Fe}^{2+}$  can be oxidised by V mL of 1 M  $\text{MnO}_4^-/\text{H}^+$  solution, calculate volume of 1 M  $\text{HNO}_2$  that can be oxidised by V mL of 1 M  $\text{MnO}_4^-/\text{H}^+$  solution.
3. Vessels made of like Al, Fe, Cr, Ni etc., can be used to store conc.  $\text{HNO}_3$ . Explain.
4. Make distinction between  $\text{NO}_3^-$  and  $\text{NO}_2^-$ .
5. What is effect of heat on  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{NO}_2$ ?
6.  $\text{NO}_2^-$  interferes in the 'ring test' of  $\text{NO}_3^-$ . How is it removed from the mixture?
7. What is hybridisation of N-atom in  $\text{HNO}_2$  and  $\text{HNO}_3$ ?
8. Complete the following in acidic medium :
  - (a)  $\text{Fe}^{2+} + \text{NO}_3^- \longrightarrow$
  - (b)  $\text{SO}_3^{2-} + \text{NO}_3^- \longrightarrow$
  - (c)  $\text{SO}_3^{2-} + \text{NO}_2^- \longrightarrow$
9. Arrange  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{SbH}_3$  in increasing:
  - (a) covalent nature
  - (b) reducing nature
  - (c) bond angle
  - (d) thermal stability
10. What is the origin of the flickering light in marshes?
11. What is the chemistry of Holme's signal?
12. What is the type of the following reaction?
 
$$\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \xrightarrow{\Delta} \text{PH}_3 + 3\text{NaH}_2\text{PO}_2$$
13. Explain reducing action of  $\text{H}_3\text{PO}_2$  and  $\text{H}_3\text{PO}_3$  with some examples.
14. Classify acids and normal salts out of :
  - (a)  $\text{NaH}_2\text{PO}_3$
  - (b)  $\text{NaH}_2\text{PO}_4$
  - (c)  $\text{NaH}_2\text{PO}_2$
  - (d)  $\text{Na}_2\text{HPO}_3$
  - (e)  $\text{Na}_2\text{HPO}_4$
15. How is phosphorus estimated?
16. (a)  $4\text{H}_3\text{PO}_3 \longrightarrow 3\text{H}_3\text{PO}_4 + \text{PH}_3$   
 (b)  $2\text{H}_3\text{PO}_2 \longrightarrow \text{H}_3\text{PO}_4 + \text{PH}_3$

Determine equivalent weights of the underlined.

## Answers

1.  $\text{HNO}_2 + \text{H}^+ + e^- \longrightarrow \text{NO} + \text{H}_2\text{O}$   
 $2\text{I}^- \longrightarrow \text{I}_2 + 2e^-$   
 $\text{Na}_2\text{S}_2\text{O}_3$  (hypo sodium thiosulphate) is used to estimate liberated  $\text{I}_2$ .  

$$2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$$
  
 $\text{HNO}_2 \equiv \text{NO} \text{ or } \text{HNO}_2 \equiv 1e^-$   
 Equivalent weight of  $\text{HNO}_2$  = molecular weight
2.  $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$  Eq. wt. =  $M/5$   
 $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-$  =  $M/1$   
 $\text{HNO}_2 + \text{H}_2\text{O} \longrightarrow \text{NO}_3^- + 3\text{H}^+ + 2e^-$  =  $M/2$   
 $V \text{ mL of } 1 \text{ M MnO}_4^- \equiv 100 \text{ mL of } 1 \text{ M Fe}^{2+}$   
 or  $V \text{ mL of } 5 \text{ N MnO}_4^- \equiv 100 \text{ mL of } 1 \text{ N Fe}^{2+}$  ... (i)  
 Also  $V \text{ mL of } 1 \text{ M MnO}_4^- \equiv V' \text{ mL of } 1 \text{ M HNO}_2$   
 $V \text{ mL of } 5 \text{ N MnO}_4^- \equiv V' \text{ mL of } 2 \text{ N HNO}_2$  ... (ii)  
 Thus, from (i) and (ii)  $V' = 50 \text{ mL}$
3. There is formation of a protective oxide layer on the surface of the metal when it reacts with  $\text{HNO}_3$ . Hence, vessels of such metals can be used to store  $\text{HNO}_3$ .
4. Add KI solution.  $\text{NO}_2^-$  would oxidise  $\text{I}^-$  to  $\text{I}_2$ .  $\text{NO}_3^-$  would give 'ring-test'.
5.  $\text{NH}_4\text{NO}_3 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$   
 $\text{NH}_4\text{NO}_2 \xrightarrow{\Delta} \text{N}_2 + 2\text{H}_2\text{O}$
6. If  $\text{NH}_4\text{Cl}$  or urea is added to a solution containing  $\text{NO}_2^-$  and  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  is decomposed as  $\text{N}_2$  and thus removed :  

$$\text{NaNO}_2 + \text{NH}_4\text{Cl} \longrightarrow \text{NaCl} + \text{N}_2 + 2\text{H}_2\text{O}$$
  

$$2\text{NaNO}_2 + \text{NH}_2\text{CONH}_2 \longrightarrow 2\text{N}_2 + \text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}$$
7.  $\text{H}-\text{O}-\ddot{\text{N}}=\text{O}$        $\text{H}-\text{O}-\text{N} \begin{matrix} \nearrow \text{O} \\ \searrow \text{O} \end{matrix}$   
 N-atom is  $sp^2$  hybridised in both.
8. (a)  $3\text{Fe}^{2+} + 4\text{H}^+ + \text{NO}_3^- \longrightarrow 3\text{Fe}^{3+} + 2\text{H}_2\text{O} + \text{NO}$   
 (b)  $\text{SO}_3^{2-} + 2\text{NO}_3^- + 2\text{H}^+ \longrightarrow \text{SO}_4^{2-} + 2\text{NO}_2 + \text{H}_2\text{O}$   
 (c)  $\text{SO}_3^{2-} + 2\text{NO}_2^- + 2\text{H}^+ \longrightarrow \text{SO}_4^{2-} + 2\text{NO} + \text{H}_2\text{O}$
9. (a) Covalent  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$   
 (b) Reducing nature  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$   
 (c) Bond angle  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$   
 $107^\circ 48' \quad 93^\circ 36' \quad 91^\circ 48' \quad 91^\circ 18'$
10.  $\text{PH}_3$  frequently contains traces of diphosphine ( $\text{P}_2\text{H}_4$ ) which causes it to catch fire spontaneously. This is the origin of the flickering light called 'will-o-the-wisp', which is sometimes seen in marshes.
11. Mixture of  $\text{CaC}_2$  and  $\text{Ca}_3\text{P}_2$  placed in the container with holes is thrown into the sea. Both react with  $\text{H}_2\text{O}$  :  

$$\text{CaC}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + \text{C}_2\text{H}_2$$
  

$$\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \longrightarrow 3\text{Ca(OH)}_2 + 2\text{PH}_3$$
  
 Some  $\text{P}_2\text{H}_4$  is also produced, which catches fire instantly, which in turn ignites  $\text{C}_2\text{H}_2$  (acetylene) and then luminous flame is produced. This guides the approaching ship. This signal is called Holme's signal.
12. In this reaction  $\text{P}_4$  (ox. no. = 0) has been reduced to  $\text{PH}_3$  (ox. no. = -3) as well as oxidised to  $\text{H}_3\text{PO}_2$  (ox. no. = +1). Hence, this is a disproportionation reaction.
13. 
$$\text{H}_3\text{PO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_3 + 2\text{H}$$
  

$$\text{H}_3\text{PO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_4 + 2\text{H}$$
  
 H produced causes reduction of salts into metals :  

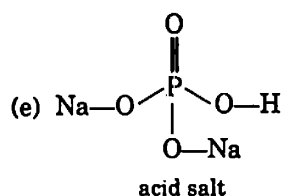
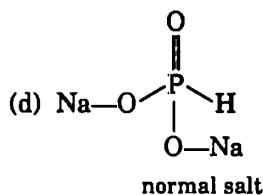
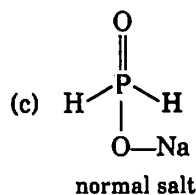
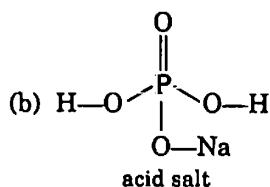
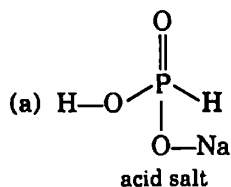
$$\text{AgNO}_3 + \text{H} \longrightarrow \text{HNO}_3 + \text{Ag}$$
  

$$\text{CuSO}_4 + \text{H} \longrightarrow \text{H}_2\text{SO}_4 + \text{Cu}$$
  

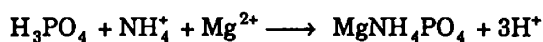
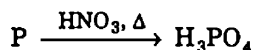
$$2\text{HgCl}_2 + 2\text{H} \longrightarrow \text{Hg}_2\text{Cl}_2 + 2\text{HCl}$$
  

$$\text{Hg}_2\text{Cl}_2 + 2\text{H} \longrightarrow 2\text{Hg} + 2\text{HCl}$$

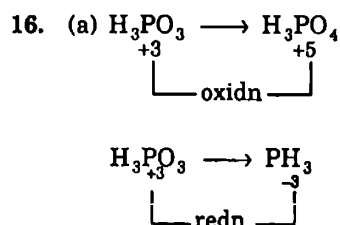
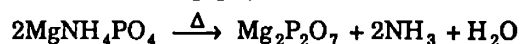
14. Salts with ionisable H (attached to O-atom) are acid salts, others are normal salts :



15. Phosphorus can be estimated by converting it into phosphates and then precipitating as  $\text{MgNH}_4\text{PO}_4$  (by adding  $\text{NH}_4\text{OH}$  and  $\text{Mg}^{2+}$ ).



On ignition, white ppt of  $\text{Mg}_2\text{P}_2\text{O}_7$  is obtained :



Equivalent weights

$$E_1 = \frac{\text{mol. wt.}}{2}$$

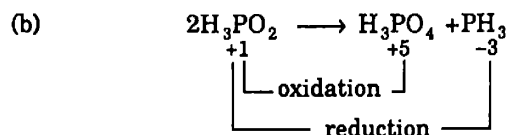
$$E_2 = \frac{\text{mol. wt.}}{6}$$

$\therefore$  Eq. wt. of  $\text{H}_3\text{PO}_3$  in disproportionation reaction

$$= E_1 + E_2$$

$$= \frac{2}{3} \text{ mol. wt.} = \frac{2}{3} \times 82$$

$$= 54.67$$



$$E_1 \text{ (oxidation)} = \frac{M}{4}$$

$$E_2 \text{ (reduction)} = \frac{M}{4}$$

$$\text{Eq. wt. (H}_3\text{PO}_2) = E_1 + E_2 = \frac{M}{2} = 33$$

Eq. wt. of (X) when it undergoes disproportionation

$$= E_1 \text{ (oxidation)} + E_2 \text{ (reduction)}$$

where,  $E_1$  (oxidation) is the eq. wt. in oxidation reaction and  $E_2$  (reduction) that of reduction reaction.

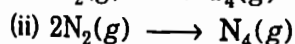
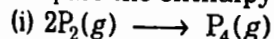
# Total Practice Set

## (Read, Plan & Solve!)

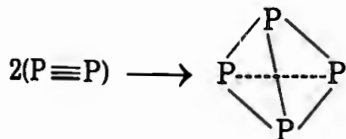
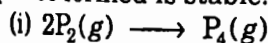
**Problem 1.** Given the following bond dissociation enthalpies ( $\text{kJ mol}^{-1}$ ):

|                          |     |
|--------------------------|-----|
| $\text{P}\equiv\text{P}$ | 490 |
| $\text{P}-\text{P}$      | 209 |
| $\text{N}\equiv\text{N}$ | 946 |
| $\text{N}-\text{N}$      | 160 |

Compare the enthalpy changes for the process

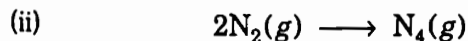


**Solution** The process involves replacement of  $2(\text{X}\equiv\text{X})$  units by 6  $\text{X}-\text{X}$  bonds in the  $\text{X}_4$  tetrahedron. Energy is released when bonds are formed and thus the species formed is stable.



$$\begin{aligned}\Delta H_f &= -6 \times \text{BE}(\text{P}-\text{P}) + 2\text{BE}(\text{P}\equiv\text{P}) \\ &= -6 \times 209 + 2 \times 490 \\ &= -274 \text{ kJ mol}^{-1}\end{aligned}$$

Formation of  $\text{P}_4$  is exothermic thus possible.



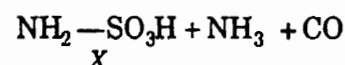
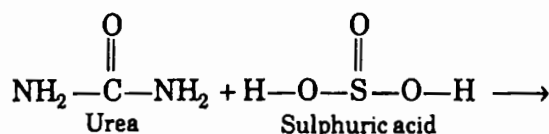
$$\begin{aligned}\Delta H_f &= -6\text{BE}(\text{N}-\text{N}) + 2\text{BE}(\text{N}\equiv\text{N}) \\ &= -6 \times 160 + 2 \times 946 \\ &= +932 \text{ kJ mol}^{-1}\end{aligned}$$

Formation of  $\text{N}_4$  is endothermic, thus is not feasible.

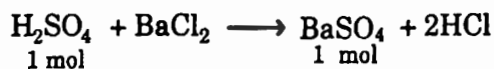
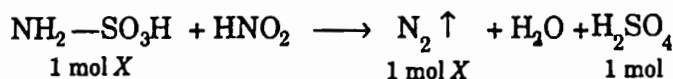
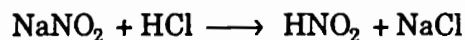
**Problem 2.** The action of concentrated sulphuric acid on urea ( $\text{NH}_2\text{CONH}_2$ ) results in the production of a white crystalline solid  $\text{X}$  of formula  $\text{H}_3\text{NO}_3\text{S}$ . This is a monobasic acid. On treatment with sodium nitrate and dilute hydrochloric acid at  $0^\circ\text{C}$  it liberates 1 mole of  $\text{N}_2$  per mol of  $\text{X}$ , and on addition of aqueous barium chloride the resulting solution yields 1 mole of  $\text{BaSO}_4$  per mol of  $\text{X}$  taken.

Deduce the structure of  $\text{X}$ .

**Solution**  $\text{NH}_2\text{CONH}_2$  (Urea) reacts with conc.  $\text{H}_2\text{SO}_4$  forming  $\text{X}(\text{H}_3\text{NO}_3\text{S})$ .  $\text{X}$  contains one ionisation H (since,  $\text{X}$  is a monobasic acid). Thus,

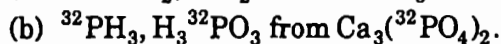
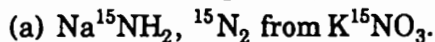


$\text{X}$  contains free  $-\text{NH}_2$  as well as free  $-\text{SO}_3\text{H}$ . ( $\text{NaNO}_2 + \text{HCl}$ ) converts free  $-\text{NH}_2$  into free  $-\text{OH}$  group liberating  $\text{N}_2$ .

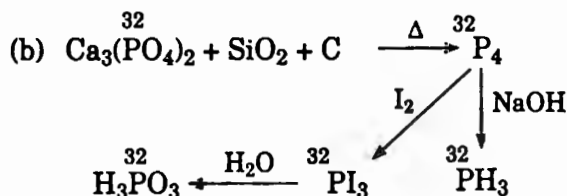
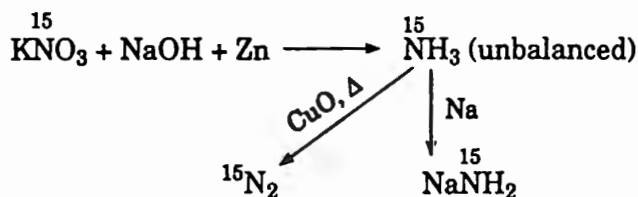


Thus,  $\text{X}$  is  $\text{NH}_2-\text{SO}_3\text{H}$  (amino sulphonic acid), 1 mole of which liberated 1 mol of  $\text{N}_2$  on reaction with ( $\text{NaNO}_2 + \text{HCl}$ ) at  $0^\circ\text{C}$  and in turn resulting solution gives 1 mole of  $\text{BaSO}_4$  on reaction with  $\text{BaCl}_2$ .

**Problem 3.** Suggest synthesis for,



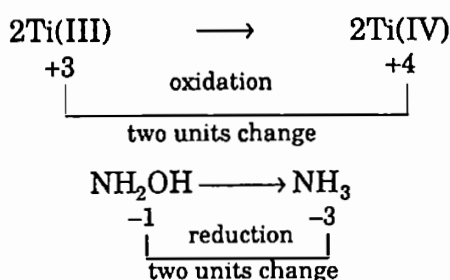
**Solution** (a) Isotopic  $^{15}\text{N}$  compounds are to be synthesised from  $\text{K}^{15}\text{NO}_3$ .



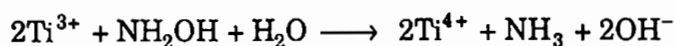
**Problem 4.** Deduce what you can about the nature of the following reactions:

- 1 mole of  $\text{NH}_2\text{OH}$  reacts with 2 moles of  $\text{Ti(III)}$  in the presence of excess alkali, and the  $\text{Ti(III)}$  is converted into  $\text{Ti(IV)}$ .
- Silver phosphite,  $\text{Ag}_2\text{HPO}_3$  is warmed with water, and the silver is precipitated as the metal.
- When 1 mole of hypophosphorous acid is treated with excess of iodine in acidic solution, 1 mole of iodine is reduced; on making the solution alkaline, another mole of iodine is consumed.

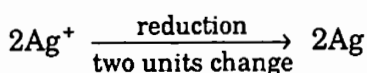
**Solution** (a) Based on change in oxidation number of two moles  $\text{Ti(III)}$  from 3 to 4,  $\text{NH}_2\text{OH}$  is reduced to  $\text{NH}_3$ .



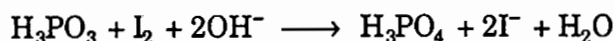
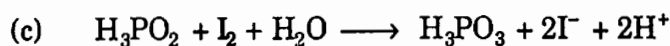
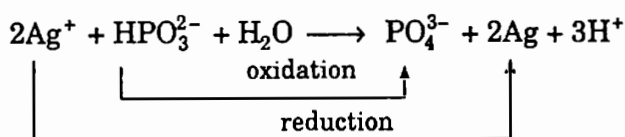
Thus,  $\text{NH}_2\text{OH}$  is reduced to  $\text{NH}_3$



- (b)  $\text{Ag}^+$  (in  $\text{Ag}_2\text{HPO}_3$ ) is reduced to  $\text{Ag}$

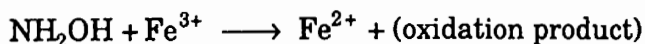


Hence,  $\text{HPO}_3^{2-}$  (oxidation number of  $\text{P} = +3$ ) should be oxidised to  $\text{PO}_4^{3-}$  (oxidation number of  $\text{P} = +5$ ) giving a change of oxidation number of two units.



**Problem 5.**  $25.0 \text{ cm}^3$  of  $0.0497 \text{ M}$  solution of  $\text{NH}_2\text{OH}$  was boiled with excess of ferric alum solution in  $\text{H}_2\text{SO}_4$ . The  $\text{Fe(II)}$  formed required  $24.7 \text{ cm}^3$  of  $0.1007 \text{ N}$   $\text{K}_2\text{Cr}_2\text{O}_7$  solution. Identify the product formed by oxidation of  $\text{NH}_2\text{OH}$ .

**Solution**  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$  which in turn is oxidised to  $\text{Fe}^{3+}$  by  $\text{Cr}_2\text{O}_7^{2-}$  in acidic medium.



$$\begin{aligned}
 \text{Equivalent of } \text{Cr}_2\text{O}_7^{2-} &= \frac{24.7 \times 0.1007}{1000} \\
 &= 0.0025
 \end{aligned}$$

$$\text{Equivalent of } \text{Fe}^{3+} \text{ or } \text{Fe}^{2+} = 0.0025$$

$$\text{Equivalent of } \text{NH}_2\text{OH} = 0.0025$$

$$\begin{aligned}
 \text{Moles of } \text{NH}_2\text{OH} (\text{taken}) &= \frac{25 \times 0.0497}{1000} \\
 &= 0.00125
 \end{aligned}$$

$$\text{Moles } (\text{NH}_2\text{OH}) = \text{Change in oxidation number}$$

$$\begin{aligned}
 &\times \text{Equivalent of } \text{NH}_2\text{OH} \\
 \therefore \text{Change in oxidation number of } \text{NH}_2\text{OH} &= \frac{0.0025}{0.00125} \\
 &= 2
 \end{aligned}$$

$$\text{Oxidation number of N in } \text{NH}_2\text{OH} = -1$$

$$\begin{aligned}
 \text{Oxidation number of N is oxidised produced} \\
 &= -1 + 2 = +1
 \end{aligned}$$

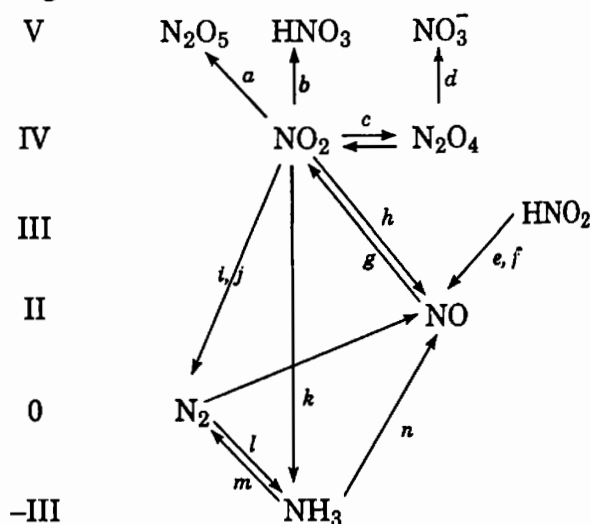
$$\text{Thus, compound formed} = \text{N}_2\text{O}$$

**Problem 6.** Give a scheme of reactions that do not involve disproportionation of the oxides of nitrogen.

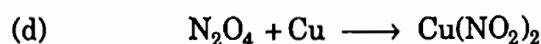
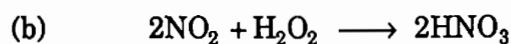
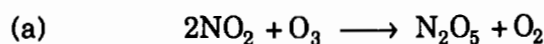
**Solution**

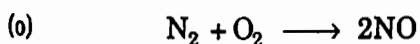
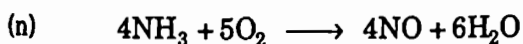
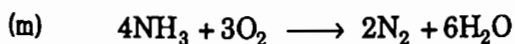
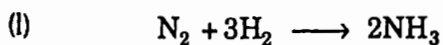
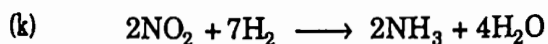
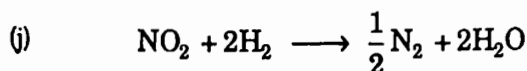
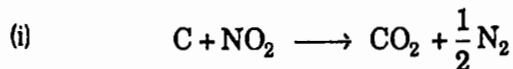
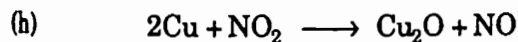
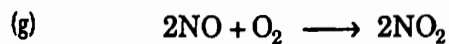
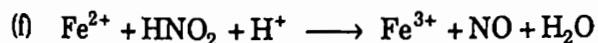
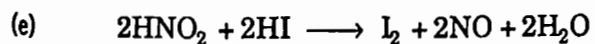
Oxidation state of

nitrogen



**Reactions :**

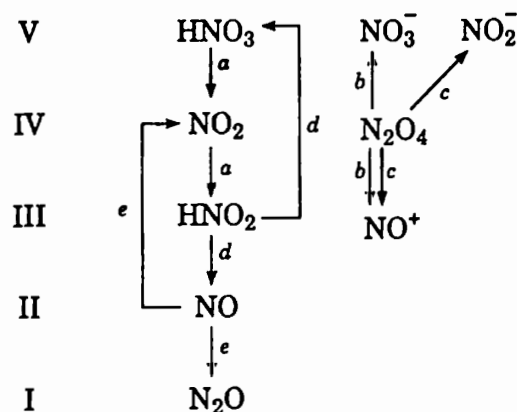




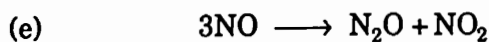
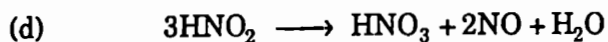
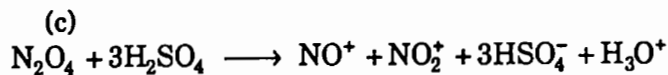
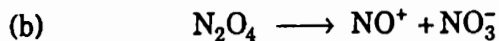
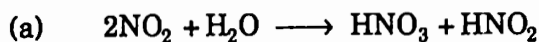
**Problem 7.** Give a scheme of reactions which involve disproportionation of the oxides of nitrogen.

### Solution

Oxidation state of  
nitrogen



Reactions :

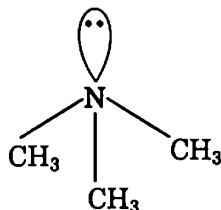




## Explanation

(a)  $(\text{SiH}_3)_3\text{N}$  is planar while  $(\text{CH}_3)_3\text{N}$  is pyramidal

- In case of  $(\text{CH}_3)_3\text{N}$ , lone pair on N and three covalent bonds with  $\text{CH}_3$  groups results in  $sp^3$  hybridisation but lone pair-bond pair repulsion causes distortion hence gives pyramidal structure :

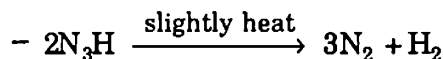


But in case of  $(\text{SiH}_3)_3\text{N}$ , lone pair on the nitrogen is transferred to the empty  $d$ -orbitals of silicon ( $p\pi$ - $d\pi$  overlap) thereby causing planarity of unit.

(b)  $\text{NF}_3$  is stable while  $\text{NCl}_3$  and  $\text{NI}_3$  are explosive

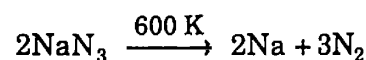
- In  $\text{NF}_3$  the electronegativity difference ( $\text{N} = 3.0$ ;  $\text{F} = 4.0$ ) permits strong  $p\pi$ - $p\pi$  bonding and the molecule is stable. But in  $\text{NCl}_3$  and  $\text{NI}_3$ , the electronegativity difference is nil or small and the molecules are unstable with  $p\pi$ - $p\pi$  bonding weak. Hence,  $\text{NF}_3$  is a stable gas,  $\text{NCl}_3$  an explosive liquid and  $\text{NI}_3$  an explosive solid.

(c) Hydrogen azide is explosive, while sodium azide is not.

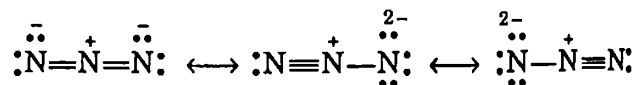


Due to increase in volume, there is explosion. Thus,  $\text{N}_3\text{H}$  is used as detonators and explosives.

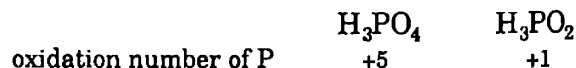
However, ionic halides are quite stable.  $\text{NaN}_3$  decomposes smoothly (but not explosively) at about 600 K



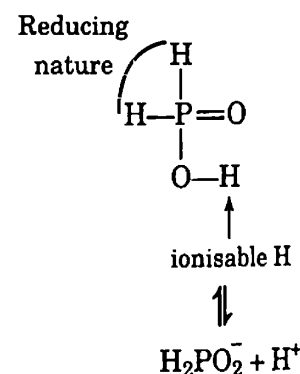
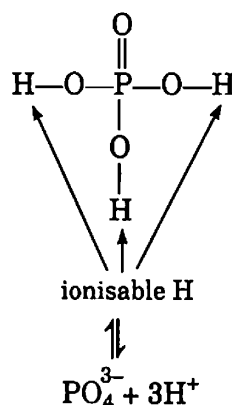
It is due to linear structure of  $\text{N}_3^-$  which is having resonating structures is stable.



(d)  $\text{H}_3\text{PO}_2$  is a powerful reducing agent but  $\text{H}_3\text{PO}_4$  is not.



$\text{H}_3\text{PO}_2$  is a monobasic acid with oxidation number of P as +1 which can be further increased to +3 and to +5. Thus,  $\text{H}_3\text{PO}_2$  can be used as a reducing agent.  $\text{H}_3\text{PO}_4$  is already in oxidised state (oxidation number of P = +5) Thus, it is not a reducing agent.  $\text{H}_3\text{PO}_4$  with all the ionisable to hydrogens is a tribasic acid and  $\text{H}_3\text{PO}_2$  with only one ionisable hydrogen is a monobasic acid. Two other hydrogen directly attached to P provide reducing nature to  $\text{H}_3\text{PO}_2$ .



# Master Exercises

## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

- Identify the group 15 (VA) elements (s) that best fits each of the following descriptions:
  - makes up part of bones and teeth
  - forms stable salts containing  $M^{3+}$  ions
  - is the most abundant element in the atmosphere
  - forms a basic oxide.
- Draw an electron-dot structure for  $N_2$ , and explain why this molecule is so unreactive?
- In the 'ring test' of  $NO_3^-$  ion, there is formation of brown colour ring. What is its formula?
- What is the nature of the nitride ion?
- Apart from  $N_2O$ , which other colourless gas supports combustion?
- Write an equation for the reaction of burning Mg with  $NO_2$ .
- Automobiles are now provided with catalytic converters. What are their role in reducing air-pollution?
- Colourless salt (A) +  $NaOH \xrightarrow{\Delta}$  gas (B) giving white fumes with  $HCl$  + alkaline solution (C)  
 $(C) + Zn \longrightarrow \text{gas (B)} \quad (A) \xrightarrow{\Delta} \underbrace{\text{gas (D) + liquid (E)}}_{\text{both triatomic}}$   
 Identify (A), (B), (C), (D) and (E).
- A few drops of concentrated ammonia solution added to a calcium bicarbonate solution causes a white precipitate to form. Write a balanced equation for the reaction.
- What is the type of the following reaction?  
 $NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$
- Identify salts (A) and (B) based on following reactions:  
 $(A) \text{ or } (B) \xrightarrow{NaOH, \Delta} NH_3 \xleftarrow{H_2O}$   
 $(A) \xrightarrow{\Delta} (C) \text{ (gas)} \xrightarrow{Al, \Delta} (D)$   
 $(B) \xrightarrow{\Delta} (E) \text{ (gas)}$   
 (E) is used as an anaesthetic.

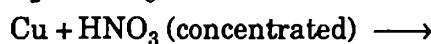
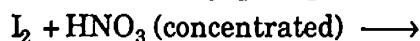
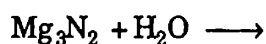
- Write balanced equation to account for each of the following observations:
  - $HNO_3$  turns brown when exposed to air
  - $HNO_3$  turns yellow-brown on standing
  - Ag dissolves in dilute  $HNO_3$ , yielding a colourless gas
  - $N_2H_4$  (hydrazine) reduces iodine to  $I^-$  and in the process is oxidised to  $N_2$  gas
- What substances form when concentrated  $HNO_3$  is reacted with  $As_2S_3$ ?
- Arrange oxides ( $M_2O_3$ ) of nitrogen family in increasing acidic nature.
- $POCl_3$ , like  $P_2O_5$ , is also used as dehydrating agent. Write reaction.
- How many (P—O) bonds are there in  $P_4O_6$  and  $P_4O_{10}$ ? (Coordinate bonds may also be included.)
- One of the oxoacid salts on heating with conc.  $HNO_3$  and ammonium molybdate gives yellow ppt. What is this ion? Give chemical reactions.
- What are structures of metaphosphoric acid and trimetaphosphoric acid?
- $H_4P_2P_7 + H_2O \longrightarrow 2H_3PO_4$   
 What conclusion can you make from this reaction regarding structure of  $H_4P_2O_7$ ?
- The structures of various phosphate and silicate anions have many similarities. Give examples.
- Starting with elemental phosphorus,  $P_4$ , show how you would prepare phosphoric acid.
- The product  $Ca(H_2PO_4)_2$  is known as triple phosphate but it is said to be richer in phosphorus than other superphosphates. Explain.
- What happens when urea slowly hydrolyses in the soil?
- Which has maximum % of (P) out of
  - superphosphate
  - triple superphosphate
  - fluoroapatite rock

## Analytical Questions

- Explain :
  - $\text{PCl}_5$  is common but  $\text{NCl}_5$  is unknown.
  - The  $\text{N}=\text{O}^+$  ion has a shorter bond length than does  $\text{NO}$ , even though the latter has an extra electron  
(Hint : compare bond order)
- Predict the structures of the following species:
  - $\text{NF}_4^+$
  - $\text{N}_2\text{F}_3^+$
  - $\text{NH}_2\text{OH}$
  - $\text{SPCl}_3$
  - $\text{PF}_3\text{Cl}_2$ .
- It has been claimed that  $\text{NH}_4\text{NO}_3$  fertiliser can be rendered unexplodable by a process that involves additives such as diammonium hydrogen phosphate  $(\text{NH}_4)_2\text{HPO}_4$ . Analysis of such a "densensitised" sample of  $\text{NH}_4\text{NO}_3$  showed the mass per cent nitrogen to be 33.81%.  
Assuming that the mixture contains only  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$ , what is the mass per cent of each of these two components?
- A mixture of the sulphides of  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$  and  $\text{Bi}_2\text{S}_3$  was treated with a  $\text{Na}_2\text{S}$  solution. Which sulphide remained undissolved? Write the equations of the sulphide dissolving reactions.
- Hyponitrous acid and nitramide both have the formula  $\text{H}_2\text{N}_2\text{O}_2$ . Hyponitrous acid is a weak diprotic acid; nitramide contains the amide group ( $-\text{NH}_2$ ). Write structures of both of these compounds.
- Peroxonitrous acid is an unstable intermediate formed in the oxidation of  $\text{HNO}_2$  by  $\text{H}_2\text{O}_2$ . It has the same formula as nitric acid,  $\text{HNO}_3$ . Show how you would expect these two acids to differ in structure?
- Determine the oxidation number of nitrogen in
  - $\text{N}_2\text{O}$
  - $\text{NO}_2$
  - $\text{HNO}_3$
  - $\text{NH}_3$
- Write the resonance Lewis structure for  $\text{N}_2\text{O}$ ,  $\text{NO}_2$  and  $\text{NO}_3^-$ .
- Illustrate how a metal such as copper can give different products with nitric acid? Give balanced equations.
- Write balanced equation(s) for the manufacture of nitric acid by the oxidation of ammonia.
- Describe the uses of ammonia and nitric acid.
- Classify the following compounds into acidic, basic and amphoteric oxides  
 $\text{SrO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{SO}_2$ ,  $\text{P}_4\text{O}_6$ ,  $\text{Cl}_2\text{O}_7$ . Write balanced equations for the reaction of each of these compounds with water, a base or an acid as the case may be.
- How far do you agree with the phenomenon concept of 'inert pair effect'? Justify your answer.
- Write balanced equations for the following reactions
  - $\text{Ca}_3\text{P}_2 + \text{H}_2\text{O} \longrightarrow$
  - $\text{P}_4\text{O}_{10} + \text{H}_2\text{O} \longrightarrow$
  - $\text{As}_4 + \text{Cl}_2$  (excess)  $\longrightarrow$
  - $\text{P}_4 + \text{KOH} + \text{H}_2\text{O} \longrightarrow$
- Describe the method for the isolation of elemental phosphorus from  $\text{Ca}_3(\text{PO}_4)_2$ .
- What is the oxidation state of phosphorus in the following?
  - $\text{H}_3\text{PO}_3$
  - $\text{PCl}_3$
  - $\text{Ca}_3\text{P}_2$
  - $\text{Na}_3\text{PO}_4$
  - $\text{POF}_3$ ?

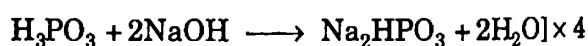
## NCERT Problems

- Give examples of compounds in which nitrogen exhibits oxidation states of  $-3$ ,  $+3$  and  $+5$ .
- Discuss the conditions required in the Haber process for the manufacture of ammonia.
- How is dinitrogen prepared in the laboratory?
- Write the products of the following reactions (give balanced equations)



- How would you prepare a sample of deuterated ammonia,  $\text{ND}_3$ ?
- Illustrate how nitrogen compounds provide good examples of multiple bonding and resonance?

- Calculate the volume of  $0.1 \text{ M}$   $\text{NaOH}$  solution required to neutralise the solution produced by dissolving  $1.1 \text{ g}$  of  $\text{P}_4\text{O}_6$  in water.



$$1.1 \text{ g P}_4\text{O}_6 = \frac{1.1}{220} = 5 \times 10^{-3} \text{ mol P}_4\text{O}_6$$

$$= 4 \times 10^{-2} \text{ mol NaOH}$$

$$\text{Let } \text{NaOH} = V \text{ mL}$$

$$\therefore \text{Moles of NaOH} = \frac{V \times 0.1}{1000}$$

$$\frac{V \times 0.1}{1000} = 4 \times 10^{-2}$$

$$\therefore V = 400 \text{ mL}$$

$$= 400 \text{ mL of } 0.1 \text{ M NaOH}$$

- Compare the structures of white phosphorus,  $\text{P}_4\text{O}_6$  and  $\text{P}_4\text{O}_{10}$ .

## Exercise 2

### (Stage 2 : High Skill Problem Solving)

#### Only One Option Correct

- Of the following acids  
I : hypo phosphorous acid  
II : hydrofluoric acid,  
III : oxalic acid  
IV : glycine  
(a) I, II are monobasic; III dibasic acid and IV amphoteric  
(b) II monobasic; I, III dibasic acid; IV amphoteric  
(c) I monobasic, II, III dibasic, IV amphoteric  
(d) I, II, III dibasic; IV amphoteric
- Following metals are soluble in aqua-regia  
(a) Pt (b) Au  
(c) Ag (d) all of these
- Which forms  $p\pi-p\pi$  multiple bonds with itself and with C and O?  
(a) P, As (b) N, As  
(c) N, P (d) N
- In  $P_4$  (tetrahedral)  
(a) each P is joined to four P  
(b) each P is joined to three P  
(c) each P is joined to two P  
(d)  $P_4$  does not exist
- Maximum number of covalent bonds formed by N and P respectively are  
(a) 3, 5 (b) 3, 6  
(c) 4, 5 (d) 4, 6
- For the hydrides of nitrogen family going down the group  
(a) stability decreases  
(b) reducing activity increases  
(c) bond angle HMM decreases  
(d) all the above variations followed
- Which of the following compounds do not exist?  
 $N_4, P_4, PCl_5, NCl_5, NCl_3, P_2O_5, NO_2, PO_2$   
(a)  $N_4, NCl_5, NO_2$  (b)  $N_4, NCl_5, PO_2$   
(c)  $PCl_5, NCl_5, PO_2$  (d) All of these
- Which of the following is/are paramagnetic?  
 $NO_2, NO, N_2O_4, N_2O_2, N_2O_5$   
(a) Only  $NO_2$  (b)  $NO_2, NO$   
(c)  $NO, NO_2, N_2O_5$  (d) All are paramagnetic
- Which of the following dibasic acids shows geometrical isomerism?  
(a) Hyponitrous acid  $H_2N_2O_2$   
(b) Maleic acid  $C_4H_4O_4$   
(c) Both (a) and (b)  
(d) None of the above
- Which is/are correct statements about  $P_4O_6$  and  $P_4O_{10}$ ?  
(a) Both form oxyacids  $H_3PO_3$  and  $H_3PO_4$  respectively  
(b) In  $P_4O_6$  each P is joined to four O and in  $P_4O_{10}$  each P is joined to six O atoms  
(c) Both (a) and (b)  
(d) None of the above
- 1 mole each of  $H_3PO_2, H_3PO_3$  and  $H_3PO_4$  will neutralise  $x$  moles of NaOH,  $y$  moles of  $Ca(OH)_2$  and  $z$  moles of  $Al(OH)_3$  (assuming all as strong electrolytes).  $x, y, z$  are in the ratio of  
(a) 3 : 1.5 : 1 (b) 1 : 2 : 3  
(c) 3 : 2 : 1 (d) 1 : 1 : 1
- The dipole moments of the given molecules are such that  
(a)  $BF_3 > NF_3 > NH_3$  (b)  $NF_3 > BF_3 > NH_3$   
(c)  $NH_3 > NF_3 > BF_3$  (d)  $NH_3 > BF_3 > NF_3$
- The electronegativities of N, C, Si and P are such that  
(a)  $P < Si < C < N$  (b)  $Si < P < N < C$   
(c)  $Si < P < C < N$  (d)  $P < Si < N < C$
- Glacial phosphoric acid is  
(a)  $HPO_3$  (b)  $H_3PO_3$   
(c)  $H_3PO_4$  (d)  $H_4P_2O_7$
- Phosgene can be obtained when  
(a) white phosphorus reacts with alkali  
(b) calcium phosphide reacts with water  
(c) chloroform reacts with air  
(d) bone comes in contact with water
- Which are acid salts?  
(a)  $NaH_2PO_2, Na_2HPO_3$  (b)  $Na_2HPO_3, Na_2HPO_4$   
(c)  $NaHCO_3, Na_2HPO_4$  (d) All of these
- Which of the following statements are true?  
(a) Cold and very dilute  $HNO_3$  forms  $NH_4NO_3$  with Zn or Sn  
(b) Concentrated  $HNO_3$  forms  $H_2SnO_3$  with Sn  
(c) Cold and more concentrated  $HNO_3$  forms  $NO_2$  with Cu  
(d) All the above are correct
- $NO_2$  is not obtained when following is heated  
(a)  $Pb(NO_3)_2$  (b)  $AgNO_3$   
(c)  $LiNO_3$  (d)  $KNO_3$
- Which is least basic?  
(a)  $NF_3$  (b)  $NCl_3$   
(c)  $NBr_3$  (d)  $NI_3$
- Which is/are used as an anaesthetic?  
(a)  $N_2O$  (b)  $C_2H_4$   
(c)  $CHCl_3$  (d) All of these

21. Which is a set of acid salts and can react with base?  
 (a)  $\text{NaH}_2\text{PO}_2$ ,  $\text{Na}_2\text{HPO}_3$ ,  $\text{NaH}_2\text{PO}_4$   
 (b)  $\text{Na}_2\text{HPO}_3$ ,  $\text{NaH}_2\text{PO}_3$ ,  $\text{Na}_2\text{HPO}_4$   
 (c)  $\text{NaHCO}_3$ ,  $\text{NaH}_2\text{PO}_3$ ,  $\text{Na}_2\text{HPO}_4$   
 (d) All of the above
22. Which is used as a rocket fuel?  
 (a)  $\text{N}_2\text{H}_4$  (b) Polybutadiene  
 (c) Both (a) and (b) (d) None of these
23.  $\text{NH}_3$  can't be obtained by  
 (a) heating of  $\text{NH}_4\text{NO}_3$  or  $\text{NH}_4\text{NO}_2$   
 (b) heating of  $\text{NH}_4\text{Cl}$  or  $(\text{NH}_4)_2\text{CO}_3$   
 (c) heating of  $\text{NH}_4\text{NO}_3$  with  $\text{NaOH}$   
 (d) reaction of  $\text{AlN}$  or  $\text{Mg}_3\text{N}_2$  or  $\text{CaCN}_2$  with  $\text{H}_2\text{O}$
24. Red and white phosphorus will differ but not in  
 (a) smell  
 (b) solubility in  $\text{CHCl}_3$   
 (c) exhibiting phosphorescence  
 (d) reactions with  $\text{HNO}_3$
25. Choose correct statements.  
 (a) Superphosphate is  $[\text{3Ca}(\text{H}_2\text{PO}_4)_2 + 7\text{CaSO}_4]$   
 (b) triple superphosphate is  $4\text{Ca}(\text{H}_2\text{PO}_4)_2$   
 (c) Both (a) and (b) are correct  
 (d) None of the above is correct
26.  $\text{N}_2\text{O}$  (laughing gas) finds use in the following except  
 (a) as a propellant for whipped ice-cream  
 (b) as an anaesthetic  
 (c) for the preparation of  $\text{N}_3\text{H}$   
 (d) as fuel for rockets
27. Following are neutral oxides except  
 (a)  $\text{NO}$  (b)  $\text{N}_2\text{O}$   
 (c)  $\text{CO}$  (d)  $\text{NO}_2$
28. Select incorrect statement about  $\text{N}_2\text{O}_4$ .  
 (a) It self ionises as  $\text{NO}^+$ ,  $\text{NO}_3^-$   
 (b) Substance containing  $\text{NO}^+$  is said to be acid and that containing  $\text{NO}_3^-$  is said to be base  
 (c)  $\text{N}_2\text{O}_4$  is paramagnetic  
 (d)  $\text{NO}_2$  dimerises to  $\text{N}_2\text{O}_4$  with disappearance in paramagnetism
29. Acid rain may cause  
 (a) rusting easier  
 (b) stone-cancer in Taj Mahal  
 (c) non-fertility of soil  
 (d) all of the above
30. Select correct statement.  
 (a) Mixture of  $\text{NH}_4\text{Cl}$  and  $\text{NaNO}_3$  on heating gives  $\text{N}_2$  gas  
 (b) CFC is used as refrigerating fluid and as propellant in aerosols  
 (c) Phosgene is formed when  $\text{P}_4$  reacts with  $\text{NaOH}$   
 (d) Phosgene dissolves in water forming  $\text{P}_2\text{O}_5$
31. 'Anhydrone' is a very effective desiccant (water absorber) used in 'dry batteries'. It is  
 (a) conc.  $\text{H}_2\text{SO}_4$  (b)  $\text{P}_2\text{O}_5$   
 (c)  $\text{CaCl}_2$  (d)  $\text{Mg}(\text{ClO}_4)_2$
32.  $\text{N}_2\text{O}$  is formed when  
 (a) moist  $\text{Fe}$  reacts with  $\text{NO}$   
 (b)  $\text{Sn}^{2+}$  reacts with conc.  $\text{HNO}_3$  in presence of  $\text{HCl}$   
 (c) cold dil.  $\text{HNO}_3$  reacts with  $\text{Cu}$  and  $\text{Zn}$   
 (d) by all the reactions
33. Which of the following compounds has the greatest ionic character?  
 (a)  $\text{PCl}_5$  (b)  $\text{SiCl}_4$   
 (c)  $\text{CCl}_4$  (d)  $\text{BCl}_3$
34.  $\text{Fe}^{3+}$  oxidises  $\text{NH}_2\text{OH}$  to  
 (a)  $\text{NO}_2$  (b)  $\text{N}_2\text{O}$   
 (c)  $\text{N}_2$  (d)  $\text{NO}$
35.  $\text{Fe}^{2+}$  reduces  $\text{NH}_2\text{OH}$  to  
 (a)  $\text{NH}_3$  (b)  $\text{N}_3\text{H}$   
 (c)  $\text{N}_2\text{H}_4$  (d)  $\text{N}_2$
36. All of the following are bases except  
 (a)  $\text{N}_2\text{H}_4$  (b)  $\text{NH}_2\text{OH}$   
 (c)  $\text{NH}_3$  (d)  $\text{N}_3\text{H}$
37. An example of an "ortho" acid is  
 (a)  $\text{HAsO}_2$  (b)  $\text{H}_3\text{AsO}_4$   
 (c)  $(\text{HPO}_3)_n$  (d)  $\text{H}_4\text{As}_2\text{O}_7$
38. Compound used in safety matches is  
 (a)  $\text{P}_4\text{S}_3$  (b)  $\text{P}_4$   
 (c)  $\text{P}_2\text{O}_5$  (d)  $\text{PCl}_3$
39. Repeated use of which one of the following fertilizers would increase the acidity of the soil?  
 (a) Urea  
 (b) Superphosphate of lime  
 (c) Ammonium sulphate  
 (d) Potassium nitrate
40. Arsenic drugs are mainly used for the treatment of  
 (a) cholera (b) typhoid  
 (c) jaundice (d) syphilis
41. The wrong statement about  $\text{N}_2\text{O}$  is  
 (a) it is nitrous oxide  
 (b) it is least reactive oxide of nitrogen  
 (c) it is not a linear molecule  
 (d) it is known as laughing gas
42. The true statement for the acids of phosphorus.  $\text{H}_3\text{PO}_2$ ,  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_4$  is  
 (a) their acidic nature is :  $\text{H}_3\text{PO}_4 < \text{H}_3\text{PO}_3 < \text{H}_3\text{PO}_2$   
 (b) all of them are reducing in nature  
 (c) all of them are tribasic acids  
 (d) the geometry of phosphorus is tetrahedral in all the three
43. The oxide which is not a reducing agent is  
 (a)  $\text{CO}_2$  (b)  $\text{NO}_2$   
 (c)  $\text{SO}_2$  (d)  $\text{ClO}_2$

44. Nitrogen is obtained by the thermal decomposition of  
 (a)  $\text{NH}_4\text{NO}_2$  (b)  $\text{NH}_4\text{NO}_3$   
 (c)  $\text{AgNO}_3$  (d)  $\text{Pb}(\text{NO}_3)_2$
45. The substance used as a fast drying agent in the laboratory is  
 (a)  $\text{Na}_2\text{PO}_4$   
 (b)  $\text{P}_2\text{O}_5$   
 (c) charcoal  
 (d) anhydrous calcium chloride
46. Laughing gas is prepared by heating  
 (a)  $\text{NH}_4\text{Cl} + \text{NaNO}_3$  (b)  $\text{NH}_4\text{Cl}$   
 (c)  $(\text{NH}_4)_2\text{SO}_4$  (d)  $\text{NH}_4\text{NO}_2$
47. The sides of safety matches contain  
 (a) red phosphorus + sand powder  
 (b)  $\text{P}_4\text{S}_3$   
 (c)  $\text{Ca}_3(\text{PO}_4)_2$  + glass pieces  
 (d)  $\text{KClO}_3$ ,  $\text{KNO}_3$ , sulphur + antimony
48. Cold solution of barium nitrite on mixing with sulphuric acid produces  
 (a)  $\text{BaSO}_4 + \text{HNO}_2$  (b)  $\text{BaSO}_4 + \text{HNO}_3$   
 (c)  $\text{BaSO}_4 + \text{NO}_2$  (d)  $\text{BaSO}_4 + \text{N}_2 + \text{O}_2$
49.  $4\text{HNO}_3 + \text{P}_4\text{O}_{10} \longrightarrow 4\text{HPO}_3 + \text{X}$   
 In the above reaction the product X is  
 (a)  $\text{NO}_2$  (b)  $\text{N}_2\text{O}_3$   
 (c)  $\text{N}_2\text{O}_4$  (d)  $\text{N}_2\text{O}_5$
50. Which of the following oxides of nitrogen is paramagnetic?  
 (a)  $\text{N}_2\text{O}$  (b)  $\text{N}_2\text{O}_5$   
 (c)  $\text{NO}_2$  (d)  $\text{N}_2\text{O}_3$
51. The structural formula of hypophosphorous acid is  
 (a)  $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{P}-\text{OH} \\ | \\ \text{H} \end{array}$  (b)  $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{P}-\text{OH} \\ | \\ \text{OH} \end{array}$   
 (c)  $\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{P}-\text{OH} \\ | \\ \text{H} \end{array}$  (d)  $\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{P}-\text{OH} \\ | \\ \text{OH} \end{array}$
52. Among the following, the paramagnetic compound is  
 (a)  $\text{Na}_2\text{O}_2$  (b)  $\text{P}_2\text{O}_5$   
 (c)  $\text{N}_2\text{O}$  (d)  $\text{KO}_2$
53. Which of the following is most acidic?  
 (a)  $\text{N}_2\text{O}_5$  (b)  $\text{P}_2\text{O}_5$   
 (c)  $\text{As}_2\text{O}_5$  (d)  $\text{Sb}_2\text{O}_5$
54. Which of the following phosphorus is the most reactive?  
 (a) Red phosphorus (b) White phosphorus  
 (c) Scarlet phosphorus (d) Violet phosphorus
55. The percentage of *p*-character in the orbitals forming P—P bonds in  $\text{P}_4$  is  
 (a) 25 (b) 33  
 (c) 50 (d) 75
56. Which blue-liquid is obtained on reacting equimolar amounts of two gases at  $-30^\circ\text{C}$ ?  
 (a)  $\text{N}_2\text{O}$  (b)  $\text{N}_2\text{O}_3$   
 (c)  $\text{N}_2\text{O}_4$  (d)  $\text{N}_2\text{O}_5$
57. Calcium cyanamide on treatment with steam produces  
 (a)  $\text{NH}_3 + \text{CaO}$  (b)  $\text{NH}_3 + \text{CaHCO}_3$   
 (c)  $\text{NH}_3 + \text{CaCO}_3$  (d)  $\text{NH}_3 + \text{Ca}(\text{OH})_2$
58. Which gas cannot be collected over water?  
 (a)  $\text{O}_2$  (b)  $\text{PH}_3$   
 (c)  $\text{N}_2$  (d)  $\text{SO}_2$
59.  $\text{NaOCl}$  reacts with  $\text{NH}_3$  to produce  
 (a)  $\text{NH}_2\text{OH}$  (b)  $\text{NH}_2\text{NH}_2$   
 (c)  $\text{N}_2$  (d)  $\text{NO}$
60. Which one of the following acid possesses oxidising, reducing and complex forming properties?  
 (a)  $\text{HNO}_3$  (b)  $\text{HCl}$   
 (c)  $\text{H}_2\text{SO}_4$  (d)  $\text{HNO}_2$
61. On hydrolysis,  $\text{PCl}_3$  gives  
 (a)  $\text{H}_3\text{PO}_3$  (b)  $\text{H}_3\text{PO}_4$   
 (c)  $\text{POCl}_3$  (d)  $\text{HPO}_3$
62. On photochemical decomposition of  $\text{HNO}_3$  the products formed are  
 (a)  $\text{NO}$  and  $\text{O}_2$  (b)  $\text{NO}_2$  and  $\text{O}_2$   
 (c)  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  (d)  $\text{N}_2\text{O}_5$  and  $\text{NO}_2$
63. Nitric oxide is formed by the reaction of  
 (a)  $\text{C} + \text{N}_2\text{O}$  (b)  $\text{Cu} + \text{HNO}_3$   
 (c)  $\text{Cu} + \text{N}_2\text{O}$  (d)  $\text{Cu} + \text{NO}_2$
64. On heating lead nitrate the product formed is  
 (a)  $\text{NO}$  (b)  $\text{NO}_2$   
 (c)  $\text{N}_2\text{O}$  (d)  $\text{N}_2\text{O}_5$
65. The number of P—O—P bonds in cyclic metaphosphoric acid is  
 (a) zero (b) two  
 (c) three (d) four
66. Polyphosphates are used as water softening agents because they  
 (a) form soluble complexes with anionic species  
 (b) precipitate anionic species  
 (c) form soluble complexes with cationic species  
 (d) precipitate cationic species
67. Solid crystalline  $\text{PCl}_5$  has structure which of the following?  
 (a) Bi-pyramidal moieties  
 (b) Octahedral and tetrahedral ions  
 (c) Square-pyramidal moieties  
 (d) Pentagonal moieties
68. Hydrazine is not  
 (a) a reducing agent (b) an oxidising agent  
 (c) an acid (d) a base

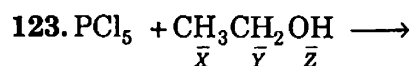
69. Which of the following oxides of nitrogen is solid?  
 (a)  $\text{NO}_2$  (b)  $\text{N}_2\text{O}$   
 (c)  $\text{N}_2\text{O}_3$  (d)  $\text{N}_2\text{O}_5$
70. The element which forms oxides in all oxidation states +1 to +5 is  
 (a) N (b) P  
 (c) As (d) Sb
71. Which of the following is arranged in the increasing order of enthalpy of vaporisation?  
 (a)  $\text{NH}_3, \text{PH}_3, \text{AsH}_3$  (b)  $\text{AsH}_3, \text{PH}_3, \text{NH}_3$   
 (c)  $\text{NH}_3, \text{AsH}_3, \text{PH}_3$  (d)  $\text{PH}_3, \text{AsH}_3, \text{NH}_3$
72. The statement true for  $\text{N}_3^-$  is  
 (a) It has non-linear structure  
 (b) It is called pseudohalogen  
 (c) the formal oxidation state of nitrogen in this anion is +1  
 (d) It is isoelectronic with  $\text{N}_2\text{O}$
73. Metallic tin and conc.  $\text{HNO}_3$  reacts to form  
 (a) metastannic acid (b) stannic nitrate  
 (c) stannous nitrite (d) stannous nitrate
74.  $\text{PI}_3$  upon hydrolysis give  
 (a) monobasic acid and dibasic acid  
 (b) monobasic acid and tribasic acid  
 (c) monobasic acid and a salt  
 (d) dibasic acid and tribasic acid
75. Common name of phosgene is  
 (a) carbon tetrachloride (b) phosphoryl chloride  
 (c) carbonyl chloride (d) phosphorus trichloride
76. The bond angle in  $\text{AsH}_3$  is greater than that in  
 (a)  $\text{NH}_3$  (b)  $\text{H}_2\text{O}$   
 (c)  $\text{BCl}_3$  (d) None of these
77. When  $\text{PCl}_3$  reacts with sulphuric acid sulphuryl chloride is formed as the final product. This shows that sulphuric acid  
 (a) has two hydroxyl groups in its structure  
 (b) is a derivative of sulphur dioxide  
 (c) is a dibasic acid  
 (d) has greater affinity for water
78. Pentavalence is phosphorus is more stable when compared to that of nitrogen even though they belong to same group is due to  
 (a) reactivity of phosphorus  
 (b) inert nature of nitrogen  
 (c) presence of  $d$ -orbital  
 (d) large size of phosphorus atom
79. Bond angle of  $109^\circ 28'$  is found in  
 (a)  $\text{NH}_3$  (b)  $\text{H}_2\text{O}$   
 (c)  $\text{CH}_5^+$  (d)  $\text{NH}_4^+$
80. What is role of phosphate ion in a detergent?  
 (a) It reduces pH of the water  
 (b) It increase pH of the water  
 (c) It removes  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions from water that causes hardness  
 (d) It increases its solubility in water
81. Among the VA(15) group elements one of them forms a compound sold under the name 'Pearl White'. The element used is  
 (a) N (b) P  
 (c) Sb (d) Bi
82. White arsenic has the chemical composition  
 (a)  $\text{As}_2$  (b)  $\text{As}_4$   
 (c)  $\text{As}_2\text{O}_5$  (d)  $\text{As}_2\text{O}_3$
83. Both  $\text{NF}_3$  and  $\text{NCl}_3$  are covalent but they differ in the extent of hydrolysis because  
 (a)  $\text{NF}_3$  is more stable than  $\text{NCl}_3$  and hydrolysis product of  $\text{NF}_3$ ,  $\text{HOF}$ , does not exist  
 (b) dipole moment of  $\text{NF}_3$  is greater than that of  $\text{NCl}_3$   
 (c) electronegativity of F is greater than that of Cl  
 (d) Cl can expand its octet by using  $d$ -orbitals
84. Nitrogen differs from P, As, Sb and Bi in the following properties  
 (a) It forms diatomic molecule  
 (b) It is not able to extend its coordination number beyond four  
 (c) Nitrogen does not function as a Lewis acid whereas P, As, Sb and Bi do so  
 (d) In all the properties given above
85.  $d\pi$ - $p\pi$  bonding is shown in  
 (a)  $\text{NO}_3^-, \text{NO}_2^-, \text{N}^{3-}, \text{CN}^-$  (b)  $\text{P}_2\text{O}_3, \text{P}_2\text{O}_5, \text{PO}_4^{3-}$   
 (c)  $\text{NH}_3, \text{PH}_3, \text{BiH}_3$  (d)  $\text{CO}, \text{NO}, \text{CO}_2, \text{NO}_2$
86. In plants, atmospheric nitrogen is converted into  
 (a) carbohydrate (b) proteins  
 (c) amino acids (d) fats
87. Pure  $\text{N}_2$  is prepared in the laboratory by heating a mixture of  
 (a)  $\text{NH}_4\text{Cl}$  and  $\text{NaOH}$  (b)  $\text{NH}_4\text{OH}$  and  $\text{NaCl}$   
 (c)  $\text{NH}_4\text{Cl}$  and  $\text{NaNO}_2$  (d)  $\text{NH}_4\text{Cl}$  and  $\text{NaNO}_3$
88. Essential constituents of plants and animal tissues are  
 (a) N and P (b) N and As  
 (c) Cu and Mg (d) Ca and Mg
89. Major minerals containing nitrogen are  
 (a) DNA (b) RNA  
 (c)  $\text{KNO}_3, \text{NaNO}_3$  (d) all of these
90. Most abundant uncombined element present in atmosphere is  
 (a) Ca (b) Mg  
 (c) Al (d) N
91. Substances burn more readily in  $\text{N}_2\text{O}$  than in air because  $\text{N}_2\text{O}$   
 (a) is reactive at high temperature  
 (b) dissociates to give  $\text{O}_2$  that supports combustion

- (c) the activation energy is increased on increasing temperature  
(d) acts as a catalyst
92. Nitric oxide is paramagnetic in  
(a) gaseous state (b) liquid state  
(c) solid state (d) polymeric state
93. Nitrosonium ion ( $\text{NO}^+$ ) is isoelectronic with  
(a) carbon dioxide (b) carbon monoxide  
(c) nitrogen dioxide (d) nitric oxide
94.  $p\pi-p\pi$  multiple bonding is present in  
(a) oxides of nitrogen (b) oxides of phosphorus  
(c) halides of nitrogen (d) halides of phosphorus
95. Paramagnetic species are  
(a)  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{O}_2$  (b)  $\text{N}_2\text{O}_2$ ,  $\text{N}_2\text{O}_4$ ,  $\text{O}_3$   
(c)  $\text{NO}^+$ ,  $\text{NO}_2^+$ ,  $\text{O}_2^+$  (d)  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$
96. With excess of  $\text{Cl}_2$  ammonia forms  
(a) ammonium chloride (b) nitrogen trichloride  
(c) nitrosyl chloride (d) nitrogen
97. The dipole moment of  $\text{NF}_3$  is less than that of  $\text{NH}_3$  because  
(a) F is more reactive than H  
(b)  $\text{NH}_3$  forms associated molecules  
(c) the resultant of the individual bond polarities is less  
(d) the resultant of the individual bond polarities is opposed by the polarity of lone pair
98.  $\text{NH}_4\text{Cl}(\text{s})$  is heated in a test tube. Vapours are brought in contact with red litmus paper, which changes to blue and then to red. It is because of  
(a) formation of  $\text{NH}_4\text{OH}$  and  $\text{HCl}$   
(b) formation of  $\text{NH}_3$  and  $\text{HCl}$   
(c) greater diffusion of  $\text{NH}_3$  than  $\text{HCl}$   
(d) greater diffusion of  $\text{HCl}$  than  $\text{NH}_3$
99. Select incorrect statement about hydrides of group 15 elements.  
(a) The central atom in the hydride is  $sp^2$  hybridised  
(b)  $\text{NH}_3$  readily form  $\text{NH}_4^+$  salts with  $\text{H}^+$ ;  $\text{PH}_3$  salts are formed with  $\text{H}^+$  under anhydrous condition  
(c) The tetrahedron is distorted due to repulsion between the lone pair of electrons and the bond pairs  
(d) The bond energy of the  $M-H$  bond decreases from  $\text{NH}_3$  to  $\text{BiH}_3$  because of increase in the size of the element
100. In liquid  $\text{NH}_3$   
(a)  $\text{NH}_4\text{Cl}$  is an acid  
(b)  $\text{NaNH}_2$  is a base  
(c)  $\text{CH}_3\text{COOH}$  behaves as strong acid  
(d) all of the above facts are true
101. A gaseous substance dissolves in water giving a pale blue solution which decolorises  $\text{KMnO}_4$  and oxidises  $\text{KI}$  to  $\text{I}_2$ . Gaseous substance is  
(a)  $\text{N}_2\text{O}_5$  (b)  $\text{NH}_3$   
(c)  $\text{N}_2\text{O}_3$  (d)  $\text{HNO}_3$
102.  $p\pi-p\pi$  multiple bonding between nitrogen atoms is present in  
(a) hyponitrous acid (b) nitrous acid  
(c) nitric acid (d) in all of these
103. In which case geometrical isomerism is not exhibited?  
(a) Hyponitrous acid (b) 2-butene  
(c) 1-butene (d) 2-pentene
104. Ambidentate ligands are  
(a)  $\text{NO}_2^-$  (b)  $\text{CN}^-$   
(c)  $\text{CNS}^-$  (d) all of these
105.  $\text{MnO}_4^-/\text{H}^+$  oxidises  $\text{NO}_2^-$  to  
(a)  $\text{N}_2$  (b)  $\text{NH}_3$   
(c)  $\text{NO}_3^-$  (d)  $\text{N}_2\text{O}$
106. A colourless salt gives a white ppt (soluble in ammonium acetate) and a brown coloured pungent gas on reaction with conc.  $\text{H}_2\text{SO}_4$ . Salt is  
(a)  $\text{Ba}(\text{NO}_3)_2$  (b)  $\text{Pb}(\text{NO}_3)_2$   
(c)  $\text{NaNO}_3$  (d)  $\text{NH}_4\text{NO}_3$
107. Nitration of aromatic compounds is done using a mixture of conc.  $\text{H}_2\text{SO}_4$  and conc.  $\text{HNO}_3$ . Intermediate formed in the nitration process is  
(a)  $\text{NO}_2^+$  (nitronium ion)  
(b)  $\text{NO}_3^-$  (nitrate ion)  
(c)  $\text{NO}^+$  (nitrosonium ion)  
(d)  $\text{NO}_2^-$  (nitrite ion)
108.  $\text{NaNO}_2$  and  $\text{NaNO}_3$  are used as food additives and generally added to meat to  
(a) retard oxidation of meat to brown coloured material  
(b) prevent growth of botulism bacteria  
(c) impart red colour to oxidised meat by  $\text{NO}$  by reaction of heme in blood  
(d) make all of the functions given above effective
109. Nitrites in water may react with amines under acidic conditions in the stomach to  
(a) give carcinogenic compounds  
(b) give proteins  
(c) keep stomach acidity free  
(d) produce free amino acids
110.  $\text{HNO}_3$  in pure state is colourless but it is often of yellow colour. It is due to  
(a) unstable structure of  $\text{HNO}_3$  which immediately changes to  $\text{NO}_2^+$   
(b) photochemical decomposition in presence of sunlight  
(c) interaction of atmospheric gases with  $\text{HNO}_3$   
(d) conversion of  $\text{HNO}_3$  into  $\text{NO}_2^+$
111. Among these ores the highest phosphorus content is in  
(a) chlorapatite (b) phosphorite  
(c) fluorspar (d) equal



112. A person working with phosphorus suffers from a disease in which bones decay. It is known as  
 (a) arthrities (b) phossy jaw  
 (c) rickets (d) cancer
113. In the preparation of red phosphorus from white phosphorus  
 (a)  $\text{MnO}_2$  is used as a catalyst  
 (b) the white phosphorus is treated in an electric furnace  
 (c) a little iodine is used as catalyst  
 (d) the gas  $\text{P}_4$  is released
114. Compound A undergoes hydrolysis to produce a colourless gas with rotten fish smell. The gas gives a vortex ring. The gas is  
 (a)  $\text{PH}_3$  (b)  $\text{P}_2\text{O}_3$   
 (c)  $\text{P}_2\text{O}_5$  (d)  $\text{P}_2\text{S}_5$
115. One of the acid listed below is formed only from  $\text{P}_2\text{O}_3$ ; the rest are formed from  $\text{P}_2\text{O}_5$ . Acid formed from  $\text{P}_2\text{O}_3$  is  
 (a)  $\text{HPO}_3$  (b)  $\text{H}_4\text{P}_2\text{O}_7$   
 (c)  $\text{H}_3\text{PO}_4$  (d)  $\text{H}_3\text{PO}_3$
116. Consider the reaction  

$$(\text{NH}_4)_2\text{HAsO}_3 + \text{CuSO}_4 \longrightarrow \underbrace{\text{CuHAsO}_3}_{\text{green ppt}} + (\text{NH}_4)_2\text{SO}_4$$
  
 The green precipitate is also known as  
 (a) Pair's green (b) Scheele's green  
 (c) Verdigris' green (d) Rinmann's green
117. A substance which gives an yellow precipitate when boiled with an excess of nitric acid and ammonium molybdate, and red precipitate with  $\text{AgNO}_3$  is  
 (a) orthophosphate (b) pyrophosphate  
 (c) metaphosphate (d) hypophosphate
118. This salt of oxoacids of phosphorus is used as washing detergent  
 (a) wavellite (b) microcosmic salt  
 (c) calgon (d) chlorapatite
119. Calgon (sodium metaphosphate) finds application as  
 (a) artificial jewel (b) paint  
 (c) a resin (d) washing powder
120. With  $\text{FeCl}_3$ , a neutral solution of orthophosphate gives an yellow precipitate insoluble in  
 (a)  $\text{CH}_3\text{COOH}$  (b)  $\text{HCl}$   
 (c)  $\text{H}_2\text{SO}_4$  (d)  $\text{NaOH}$
121. Phosphorus trichloride,  $\text{PCl}_3$ , undergoes hydrolysis to produce an oxoacid. It has the formula  
 (a)  $\text{HPO}_3$  (b)  $\text{H}_3\text{PO}_3$   
 (c)  $\text{H}_3\text{PO}_4$  (d)  $\text{H}_3\text{PO}_2$
122. The solid  $\text{PCl}_5$  exists as  
 (a)  $\text{PCl}_3$  (b)  $\text{PCl}_4^+$   
 (c)  $\text{PCl}_6^-$  (d)  $\text{PCl}_4^+$  and  $\text{PCl}_6^-$



In the above reaction Cl replaces one of the H-atoms in  $\text{CH}_3\text{CH}_2\text{OH}$ . This H is of

- (a) C (in  $\bar{X}$ ) (b) C (in  $\bar{Y}$ )  
 (c) O (in  $\bar{Z}$ ) (d) any of X, Y and Z
124. The high reactivity and low volatility of white phosphorus is due to  
 (a) tetrahedrally arranged  $\text{P}_4$  units  
 (b) bond angle of  $60^\circ$   
 (c) weak van der Waals' force of attraction  
 (d) increased steric (strain) factor
125. Stability of pentahalides is in order  
 (a)  $\text{P} > \text{Sb} > \text{As} > \text{Bi}$  for given X  
 (b)  $\text{F} > \text{Cl} > \text{Br}$  for given element  
 (c) both (a) and (b)  
 (d) None of the above

### One or More Than One Options Correct

- $\text{N}_2\text{H}_4$  and  $\text{H}_2\text{O}_2$  show similarity in  
 (a) hybridisation of central atoms  
 (b) oxidising nature  
 (c) reducing nature  
 (d) molar mass
- In acidic medium  $\text{N}_2\text{H}_4$   
 (a) is oxidised to  $\text{N}_2$   
 (b) loses four electrons  
 (c) has equivalent mass 8  
 (d) reduces  $\text{AuCl}_3$  to  $\text{AuCl}$
- $\text{N}_2\text{H}_4$  reduces  $\text{IO}_3^-/\text{H}^+$   
 (a) to  $\text{I}^+$   
 (b) with  $\text{I}_2$  as an intermediate indicated by violet colour in  $\text{CCl}_4$  layer  
 (d) indicated by blue colour with starch  
 (d) to  $\text{I}^-$
- $\text{N}_2\text{H}_4$   
 (a) is an endothermic compound  
 (b) burns in air with evolution of heat in an exothermic compound  
 (c) is kinetically stable  
 (d) reduces  $\text{FeCl}_3$  to  $\text{FeCl}_2$  in acidic medium
- Thermodynamic tendency of  $\text{PH}_3(g)$  to react with  $\text{HX}(g)$  would be favoured by  
 (a) low H—X bond energy  
 (b) high electron affinity of X  
 (c) high lattice energy of  $\text{PH}_4\text{X}(s)$   
 (d) high electronegativity of P
- The following side reaction in the production of  $\text{N}_2\text{H}_4$   

$$\text{N}_2\text{H}_4 + 2\text{NH}_2\text{Cl} \longrightarrow \text{N}_2 + 2\text{NH}_4\text{Cl}$$
  
 (a) is catalysed by traces of heavy metals as  $\text{Cu}^{2+}$   
 (b) is suppressed by addition of gelatin or glue

- (c) is made reversible by removing  $N_2$   
 (d) is made reversible by adding NaOH

7.  $NH_2OH$  can be used as

- (a) on oxidising agent  
 (b) a reducing agent  
 (c) an autioxidant in photographic developers  
 (d) oxime forming reagent (with carbonyl compound)

8. Select correct statement(s).

$NH_2OH$  forms *syn* and *anti* isomer with

- (a) benzaldehyde (b) acetone  
 (c) acetaldehyde (d) benzophenone

9. Nylon-6 is formed from caprolactam which is formed from

- (a) cyclohexanone and hydroxyl amine  
 (b) cyclohexanone and hydrazine  
 (c) benzophenone and hydrazine  
 (d) benzophenone and hydroxylamine

10. Select correct statement(s).

- (a)  $SbCl_3$  is hydrolysed to orange  $SbOCl$  soluble in dil. HCl  
 (b)  $BiCl_3$  is hydrolysed to white  $BiOCl$  soluble in dil. HCl  
 (c)  $PCl_5$  can change to  $PCl_6^-$  and  $PCl_4^+$  with no change in hybridisation of P.  
 (d)  $NCl_5$  and  $PCl_5$  are stable compounds.

2. Bond energy of

$$(N \equiv N) = 946 \text{ kJ mol}^{-1}$$

$$(P \equiv P) = 481 \text{ kJ mol}^{-1}$$

$$(N - N) = 160 \text{ kJ mol}^{-1}$$

$$(P - P) = 215 \text{ kJ mol}^{-1}$$

which molecules do not exist?

- (a)  $P_4$  (b)  $N_4$   
 (c)  $N_2$  (d)  $P_2$

3. Following table compares properties of red phosphorus and white phosphorus. Which is incorrect comparison?

| Red                                      | White                                           |
|------------------------------------------|-------------------------------------------------|
| (a) Nontoxic and has polymeric structure | Toxic, waxy discrete tetrahedral $P_4$ molecule |
| (b) Discrete tetrahedral molecule        | $P_4$ Polymeric structure                       |
| (c) High m.p., less reactive             | Low m.p., more reactive                         |
| (d) Shows no phosphorescence in air      | Shows phosphorescence in air                    |

4. In  $P_4$  (tetrahedral)

- (a) each P is joined to four P  
 (b) each P is joined to three P  
 (c) each P is joined to two P  
 (d)  $P_4$  does not exist

5. High reactivity of white phosphorus is due to

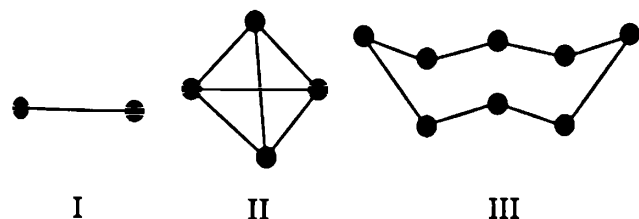
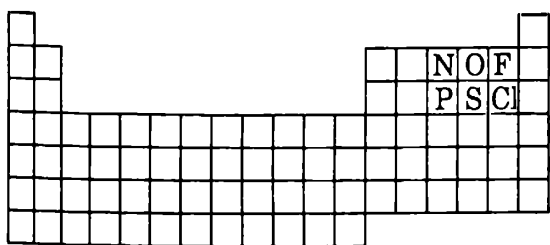
- (a) unusual bonding that produces considerable strain  
 (b) high solubility in water  
 (c) oxide layer made on it  
 (d) all of the above

6. White phosphorus reacts with NaOH forming  $PH_3$  and  $H_2PO_2^-$ . This is an example of

- (a) neutralisation  
 (b) thermal decomposition  
 (c) redox reaction  
 (d) disproportionation

### Passage 1

Consider the six second and third-row elements in group 15–17 of the Periodic Table. Possible molecular structures for common allotropes of these elements are shown below:

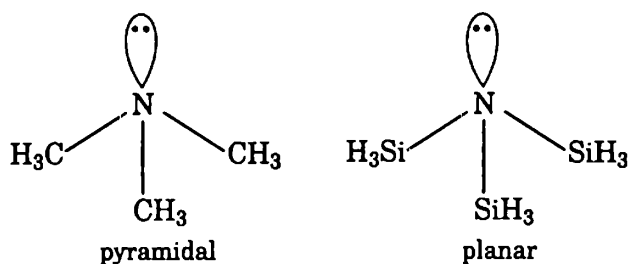


1. Following is the matching of the structure of molecular form. Which is not the correct matching?

- (a) Nitrogen I (b) Phosphorus II  
 (c) Sulphur III (d) Ozone I

### Passage 2

Question given below is based on the following structures:



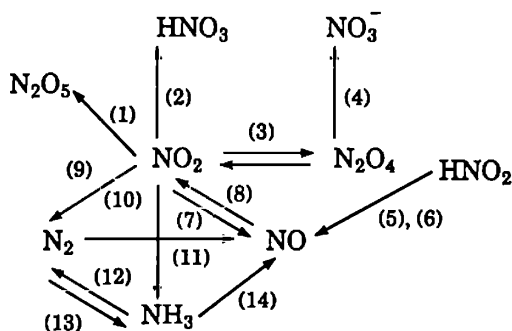
1. Structures of  $N(CH_3)_3$  and  $N(SiH_3)_3$  are different. It is due to the fact that

- (a) silicon also uses *d*-orbitals in multiple bonding

- (b) in case of  $N(\text{SiH}_3)_3$ , lone pair of N-atom is transferred to the empty  $d$ -orbitals of silicon ( $p\pi-d\pi$  overlapping)  
 (c) both of the above  
 (d) none of the above

### Passage 3

Consider following scheme involving oxides and oxy-acids of nitrogen. Based on this answer the questions given at the end.



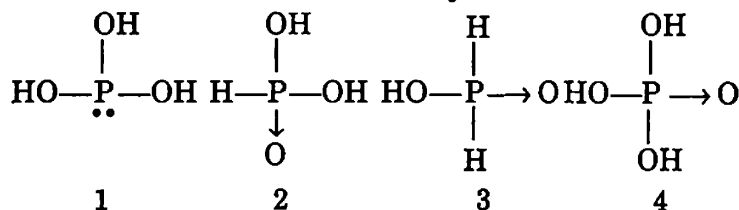
- Out of the following which reactions are disproportionations?  
 (a) 2, 10 (b) 2, 3  
 (c) 1, 11 (d) 13, 14
- In which case change in oxidation number is maximum?  
 (a) 1 (b) 10  
 (c) 5 (d) 11

### Passage 4

Questions given below are based on the following experiment.

An oxyacid of phosphorus has the following properties  
 Complete neutralisation of the acid with sodium hydroxide solution gives an aqueous solution of sodium ions and oxy-acid anions in the ratio 2 : 1. When a solution of the acid is warmed with silver nitrate solution metallic silver is deposited.

1. What is the structure of the oxy-acid?

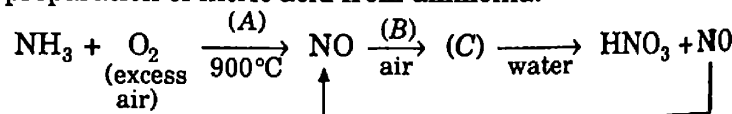


- (a) 1 (b) 2  
 (c) 3 (d) 4
2. This oxy-acid is converted into ..... on reaction with acetic anhydride  
 (a)  $(\text{CH}_3\text{CO})_2\text{HPO}_4$  (b)  $(\text{CH}_3\text{CO})_2\text{HPO}_3$   
 (c)  $\text{P}_2\text{O}_3$  (d)  $\text{P}_2\text{O}_5$
3. pH of 0.01 M solution of the sodium salt of this acid formed (assume  $\text{p}K_{a1} = 2x$ ) is

- (a)  $6 + 2x$  (b)  $6 - 2x$   
 (c)  $6 - x$  (d)  $6 + x$

### Passage 5

The following flow diagram represents the industrial preparation of nitric acid from ammonia:



Answer the questions given below

1. Which line of entry describes the undefined reagents, products and reaction conditions?

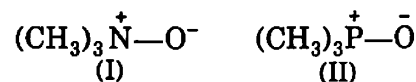
| A                          | B                            | C                      |
|----------------------------|------------------------------|------------------------|
| (a) Catalyst               | cool ( $-25^\circ\text{C}$ ) | $\text{NO}_2$          |
| (b) Catalyst               | cool ( $-25^\circ\text{C}$ ) | $\text{N}_2\text{O}$   |
| (c) Catalyst               | high pressure                | $\text{NO}_2$          |
| (d) High pressure catalyst |                              | $\text{N}_2\text{O}_3$ |

2. Formation of  $\text{HNO}_3$  when (C) is dissolved in  $\text{H}_2\text{O}$  takes place through various reactions. Select the reaction not observed in this step.

- (a)  $\text{NO}_2 + \text{H}_2\text{O} \longrightarrow \text{HNO}_3 + \text{HNO}_2$   
 (b)  $\text{HNO}_2 \longrightarrow \text{H}_2\text{O} + \text{NO} + \text{NO}_2$   
 (c)  $\text{NO}_2 + \text{H}_2\text{O} \longrightarrow \text{HNO}_3 + \text{NO}$   
 (d) None of the above

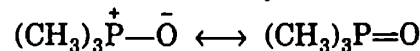
### Passage 6

Trimethylamine oxide and trimethyl phosphine oxide can be represented as



Answer the following questions based on these

1. Select correct structure.  
 (a)  $(\text{CH}_3)_3\text{N}=\text{O}$  (b)  $(\text{CH}_3)_3\text{P}=\text{O}$   
 (c) both (a) and (b) (d) None of these
2. Trimethyl phosphine oxide can be represented by two canonical forms but trimethylamine oxide can't be

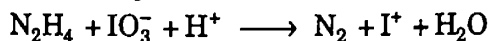


It is due to

- (a) phosphorus accepts charge density from oxygen and accommodates it in its vacant  $d$ -orbitals  
 (b) nitrogen does not possess  $d$ -orbitals and thus can't form the  $\pi$ -bonded structure  
 (c) both (a) and (b)  
 (d) None forms canonical forms
3. Trimethyl phosphine oxide is stable because  
 (a) it has two resonating structure  
 (b) phosphorus-oxygen double bond has high dissociation energy  
 (c) both (a) and (b)  
 (d) None of the above

**Passage 7**

$\text{N}_2\text{H}_4$  reduces  $\text{IO}_3^-$  to  $\text{I}^+$  in acidic medium.



Answer the following questions

1. Equivalent mass of  $\text{N}_2\text{H}_4$  (molar mass =  $42 \text{ g mol}^{-1}$ ) is  
(a) 42 (b) 21  
(c) 10.5 (d) 14
2. Equivalent mass of  $\text{KIO}_3$  (molar mass =  $214 \text{ g mol}^{-1}$ ) is  
(a) 71.33 (b) 107.0  
(c) 214.0 (d) 53.5
3. Intermediate in the above reaction is  $\text{I}_2$  which can be detected by  
(a) taking solvent  $\text{CCl}_4$  in which  $\text{I}_2$  is soluble and thus layer becomes violet  
(b) starch as indicator which turns blue  
(c) both (a) and (b)  
(d) None of the above
4.  $\text{N}_2\text{H}_4$  is oxidised to  $\text{N}_2$ . Both N-atom in  $\text{N}_2$  are from  $\text{N}_2\text{H}_4$ . It can be verified by  
(a) taking  $^{15}\text{N}$  enriched  $\text{N}_2\text{H}_4$ ,  
(b) taking  $^2\text{D}$  enriched  $\text{N}_2\text{H}_4$   
(c) taking both (a) & (b)  
(d) taking none of the above

**Assertion & Reason**

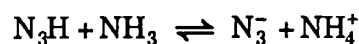
Codes :

- (a) Both **A** and **R** are true and **R** is the correct explanation of **A**.
  - (b) Both **A** and **R** are true but **R** is not the correct explanation of **A**.
  - (c) **A** is true but **R** is false.
  - (d) **A** is false but **R** is true.
1. **Assertion (A)** : On cooling, the brown colour of  $\text{NO}_2$  disappears.  
**Reason (R)** : On cooling  $\text{NO}_2$  forms dimer ( $\text{N}_2\text{O}_4$ ) resulting in the pairing of the odd electrons in  $\text{NO}_2$ .
  2. **Assertion (A)** : Both  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_4$  have the same number of hydrogen atoms but  $\text{H}_3\text{PO}_4$  is a tribasic acid and  $\text{H}_3\text{PO}_3$  is a dibasic acid.  
**Reason (R)** : 1 mole of  $\text{H}_3\text{PO}_3$  is neutralised by 2 moles of  $\text{NaOH}$  while 1 mole of  $\text{H}_3\text{PO}_4$  is neutralised by 3 moles of  $\text{NaOH}$ .
  3. **Assertion (A)** :  $\text{N}_2\text{H}_4$  is kinetically stable compound.  
**Reason (R)** : Two N-atoms are bonded by triple bonds.
  4. **Assertion (A)** :  $\text{N}_3\text{H}$  explodes violently on slight heating.  
**Reason (R)** :  $\text{N}_3^-$  has linear structure and is stable due to resonance.

5. **Assertion (A)** :  $\text{N}_2\text{H}_4$  is a weaker base than  $\text{NH}_3$ .

**Reason (R)** : Its behaviour is bifunctional.

6. **Assertion (A)** : Equivalent mass of  $\text{N}_2\text{H}_4$  is 8 in acidic medium or basic medium.  
**Reason (R)** : It is oxidised to  $\text{N}_2$  with loss of four electron per  $\text{N}_2\text{H}_4$  unit.
7. **Assertion (A)** :  $\text{IO}_3^-$  is reduced to  $\text{I}^+$  but intermediate gives violet colour in  $\text{CCl}_4$  (taken as medium).  
**Reason (R)** :  $\text{I}_2$  is formed as the intermediate.
8. **Assertion (A)** : Each N-atom is  $sp^3$ -hybridised in  $\text{N}_2\text{H}_4$ .  
**Reason (R)** : It has *gauche* conformation.
9. **Assertion (A)** :  $\text{H}_2\text{O}_2$  and  $\text{N}_2\text{H}_4$  have oxidant and reductant nature.  
**Reason (R)** : Both have equivalent mass of 8.
10. **Assertion (A)** :  $\text{N}_3\text{H}$  is a weak acid and  $\text{NH}_3$  is a weak base.  
**Reason (R)** : There is proton-donor acceptor equilibrium

**True & False**

1.  $\text{H}_3\text{PO}_2$  is a weak monobasic acid.
2.  $\text{N}_3\text{H}$  is a stronger acid than acetic acid.
3.  $\text{N}_3\text{H}$  is thermodynamically stable.
4.  $\text{N}_3^-$  has linear structure.
5.  $\text{N}_2\text{H}_4$  is thermodynamically endothermic compound but is kinetically stable.
6.  $\text{P}_4\text{O}_{10}$  changes malonic acid into  $\text{CO}_2$ .
7.  $\text{NaH}_2\text{PO}_2$  and  $\text{NaHPO}_3$  are acid salts.
8.  $\text{Na}_3\text{PO}_4$  and  $\text{NaHPO}_3$  are normal salts.
9.  $\text{NH}_3$ ,  $\text{PH}_3$  and  $\text{AsH}_3$  have  $sp^3$ -hybridised central atom and thus each has bond angle of  $109^\circ 28'$ .
10.  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{CO}_3$  give  $\text{NH}_3$  gas on heating.
11.  $\text{N}_2\text{O}$  resembles molecular  $\text{O}_2$  since, it supports combustion.
12. Structure of  $\text{N}_2\text{O}$  is similar to that of  $\text{CO}_2$ .
13. N—O bond length in  $\text{N}_2\text{O}_4$  is greater than expected due to charge repulsion.
14.  $\text{H}_2\text{N}_2\text{O}_2$  exists as *cis* and *trans* geometrical isomer.
15.  $\text{NaNO}_2$  and  $\text{NaNO}_3$  are used as food additives and generally added to meat.

## Fill in the Blanks

1. When mixture of  $\text{NH}_4\text{Cl}$  and  $\text{NaNO}_2$  is heated, gaseous product formed is .....
2. Formation of  $\text{N}_2\text{H}_4$  is an ..... reaction but combustion is an ..... reaction.
3. Out of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}$ , paramagnetic species are .....
4.  $\text{N}_2\text{H}_4$  is ..... stable compound.
5.  $\text{N}_2\text{H}_4$  is a ..... base than  $\text{NH}_3$  and  $\text{N}_3\text{H}$  is a ..... acid than  $\text{CH}_3\text{COOH}$ .
6.  $\text{N}_2\text{H}_4$  is oxidised to ..... in acidic medium and to ..... in basic medium.
7.  $\text{N}_3^-$  is stable due to .....
8.  $\text{H}_3\text{PO}_4$  is a ..... acid,  
 $\text{H}_3\text{PO}_3$  is a ..... acid and  
 $\text{H}_3\text{PO}_2$  is a ..... acid
9. Reducing nature of  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_2$  is in order .....
10.  $\text{N}_2\text{O}$ ,  $\text{NO}$  are .....  $\text{As}_4\text{O}_6$ ,  $\text{As}_4\text{O}_{10}$  are .....  
 $\text{Bi}_2\text{O}_3$  is a .....
11. Out of  $\text{PCl}_3$ ,  $\text{PCl}_5$ ,  $\text{NCl}_5$  and  $\text{NCl}_3$ , least stable is .....
12.  $\text{As}^{3+}$  salts are ..... white  $\text{Bi}^{5+}$  salts are .....
13. If  $\text{MCl}_3$  is hydrolysed and there is an orange turbidity then  $\text{MCl}_3$  is ..... and when there is white turbidity then  $\text{MCl}_3$  is .....
14.  $\text{N}_3^-$  resembles ..... and is also called .....
15.  $\text{N}_2\text{H}_4$  can be prepared by .....

## Matrix-Match Type Questions

### I. Only One Correct

1. Match the acids (in List I) with number of acid salts formed by them (in List II).

| List I                  |    | List II |
|-------------------------|----|---------|
| A. Hypophosphorus acid  | 1. | Two     |
| B. Orthophosphorus acid | 2. | Zero    |
| C. Orthophosphoric acid | 3. | One     |
| D. Mclitic acid         | 4. | Five    |

2. Match the reactions of metals with dilute  $\text{HNO}_3$  (in List I) with the nitrogen compounds (obtained by oxidation/reduction (in List II).

| List I                             | List II                     |
|------------------------------------|-----------------------------|
| A. $\text{Mg} + \text{dil. HNO}_3$ | 1. $\text{NO}$              |
| B. $\text{Zn} + \text{dil. HNO}_3$ | 2. $\text{H}_2$             |
| C. $\text{Sn} + \text{dil. HNO}_3$ | 3. $\text{N}_2\text{O}$     |
| D. $\text{Pb} + \text{dil. HNO}_3$ | 4. $\text{NH}_4\text{NO}_3$ |

3. Match the compounds (in List I) with their oxidation number of N (in List II).

| List I                    | List II |
|---------------------------|---------|
| A. $\text{N}_2\text{H}_4$ | 1. -1   |
| B. $\text{NH}_2\text{OH}$ | 2. 3    |
| C. $\text{HNO}_2$         | 3. 4    |
| D. $\text{NO}_2$          | 4. 5    |
| E. $\text{HNO}_3$         | 5. -2   |

### II. One or More Correct

1. Match the reaction in Column I with their corresponding characteristic(s) in Column II.

| Column I                                                                                                                           | Column II                                                      |
|------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------|
| A. $3\text{H}_3\text{PO}_2 \longrightarrow 2\text{H}_3\text{PO}_3 + \text{PH}_3$                                                   | 1. Disproportionation                                          |
| B. $2\text{NO}_2 + \text{H}_2\text{O} \longrightarrow \text{HNO}_3 + \text{HNO}_2$                                                 | 2. Reducing nature of any reactant                             |
| C. $\text{H}_3\text{PO}_4 + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaHPO}_4 + 2\text{H}_2\text{O}$                           | 3. Dibasic acid                                                |
| D. $2\text{NH}_2\text{OH} + 4\text{CuO} \longrightarrow \text{Cu}_2\text{O} \downarrow + \text{N}_2\text{O} + 3\text{H}_2\text{O}$ | 4. Equivalent weight (reactant) $\text{mol. wt} = \frac{4}{4}$ |
|                                                                                                                                    | 5. Reactant is paramagnetic                                    |
|                                                                                                                                    | 6. Oxidising nature of any reactant                            |

2. Match the half-reactions in Column I with the corresponding characteristic(s) in Column II.

| Column I                                                                                | Column II                                               |
|-----------------------------------------------------------------------------------------|---------------------------------------------------------|
| A. $\text{N}_2\text{H}_5^+ \longrightarrow \text{N}_2 + 5\text{H}^+$                    | 1. Oxidation                                            |
| B. $\text{N}_2\text{H}_4 + \text{OH}^- \longrightarrow \text{N}_2 + \text{H}_2\text{O}$ | 2. Reduction                                            |
| C. $2\text{N}_3^- \longrightarrow 3\text{N}_2$                                          | 3. Equivalent weight<br>= $\frac{\text{molar mass}}{4}$ |
| D. $\text{NH}_2\text{OH} \longrightarrow \text{NH}_3$                                   | 4. Equivalent weight<br>= $\frac{\text{molar mass}}{2}$ |
| E. $\text{NH}_2\text{OH} \longrightarrow \text{N}_2\text{O}$                            | 5. Exchange of 4 electrons                              |
|                                                                                         | 6. Exchange of 2 electrons                              |

3. Match the species in Column I with their characteristic(s) in Column II.

| Column I                     | Column II                                  |
|------------------------------|--------------------------------------------|
| A. $\text{NH}_2\text{OH}$    | 1. Reducing agent                          |
| B. $\text{N}_3\text{H}$      | 2. Oxidising agent                         |
| C. $\text{NH}_2-\text{NH}_2$ | 3. Weak base                               |
| D. $\text{NH}_3$             | 4. Molecule or anion with linear structure |
| E. $\text{N}_2\text{O}$      | 5. Isoelectronic of $\text{CO}_2$          |

### Integer Answer Types

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the ORS have to be darkened. For example, if the correct answers to question number X, Y, Z and W (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will like the following :

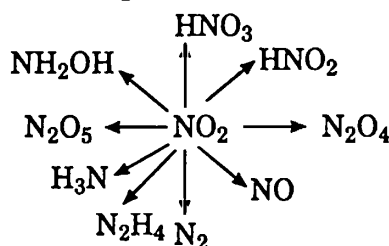
| X | Y | Z | W |
|---|---|---|---|
| ① | ① | ① | ① |
| ② | ② | ② | ② |
| ③ | ③ | ③ | ③ |
| ④ | ④ | ④ | ④ |
| ⑤ | ⑤ | ⑤ | ⑤ |
| ⑥ | ⑥ | ⑥ | ⑥ |
| ⑦ | ⑦ | ⑦ | ⑦ |
| ⑧ | ⑧ | ⑧ | ⑧ |
| ⑨ | ⑨ | ⑨ | ⑨ |

### Set I

- How many of the species are isoelectronic?  
 $\text{N}_2\text{O}, \text{CO}_2, \text{CN}_2^{2-}, \text{N}_3^-, \text{NH}_2\text{OH}, \text{N}_3\text{H}$
- How many of the species are paramagnetic?  
 $\text{N}_2\text{O}, \text{NO}, \text{NO}_2, \text{O}_2, \text{NO}_2^+, \text{NO}^+, \text{CO}^+$
- In the following, equilibrium partial pressure of  $\text{NH}_3$ ,  $\text{N}_2$  and  $\text{H}_2$  gases are 4, 1 and 2 atm respectively at 300 K. What is value of  $K_p$ ?  
$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
- In the oxidation of  $\text{N}_2\text{H}_4$  to  $\text{N}_2$ , equivalent weight of  $\text{N}_2\text{H}_4$  would be .....
- Total number of  $\sigma$  bonds in  $\text{N}_3\text{H}$  is .....
- $\text{NO}_3^-$  is reduced to  $\text{NH}_4^+$ . What is change in oxidation number?
- A phosphate mineral has formula  $\text{Ca}_x\text{P}_3\text{O}_{12}\text{F}$ . Thus  $x$  is .....
- How many species out of the following have reducing properties?  
 $\text{NH}_3, \text{PH}_3, \text{H}_3\text{PO}_2, \text{H}_3\text{PO}_3, \text{H}_3\text{PO}_4, \text{LiAlH}_4, \text{BH}_3$

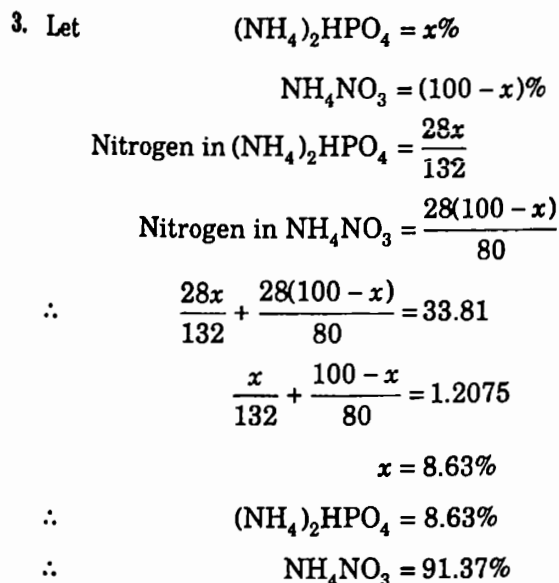
### Set II

- How many POP bonds are there in  $\text{P}_4\text{O}_{10}$ ?
- How many P—H bonds are there in  $\text{H}_3\text{PO}_2$ ?
- In  $\text{PCl}_5$ , how many (P—Cl) are inclined at  $120^\circ$  with one each.
- 25.0 mL of 0.05 M solution of  $\text{NH}_2\text{OH}$  was boiled with excess of  $\text{Fe}^{3+}$  in acidic medium. The  $\text{Fe}^{2+}$  formed required 25.0 mL of 0.1 N  $\text{Cr}_2\text{O}_7^{2-}$  in acidic medium. What is oxidation number of the N in new product?
- What is pH of 0.01 M  $\text{Na}_2\text{HPO}_4$  if  $\text{p}K_a$  is 6?
- Consider following reactions :

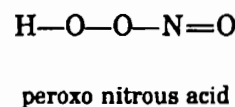
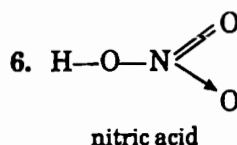
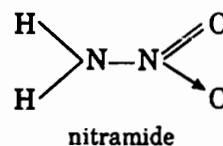
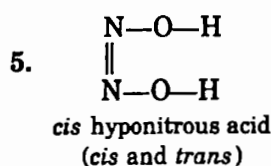
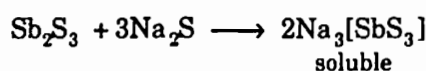
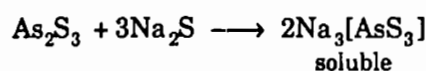


- In how many reactions  $\text{NO}_2$  has been oxidised?
- In how many reactions  $\text{NO}_2$  has been reduced in Q. 7?
  - Maximum change in oxidation number of nitrogen is .....

(c) Pyramidal at N and bent at O (d) Tetrahedral  
(e) Trigonal bipyramidal with apical Cl atom.



4.  $\text{Bi}_2\text{S}_3$  remains undissolved



## NCERT Problems

Refer text

## Exercise 2

### Only One Option Correct

- |          |          |          |          |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 1. (c)   | 2. (d)   | 3. (d)   | 4. (b)   | 5. (a)   | 6. (d)   | 7. (b)   | 8. (b)   | 9. (c)   | 10. (c)  |
| 11. (d)  | 12. (c)  | 13. (c)  | 14. (c)  | 15. (c)  | 16. (c)  | 17. (d)  | 18. (d)  | 19. (a)  | 20. (d)  |
| 21. (c)  | 22. (c)  | 23. (a)  | 24. (d)  | 25. (c)  | 26. (d)  | 27. (d)  | 28. (c)  | 29. (d)  | 30. (a)  |
| 31. (d)  | 32. (d)  | 33. (b)  | 34. (b)  | 35. (a)  | 36. (d)  | 37. (b)  | 38. (a)  | 39. (c)  | 40. (d)  |
| 41. (c)  | 42. (d)  | 43. (a)  | 44. (a)  | 45. (d)  | 46. (a)  | 47. (b)  | 48. (a)  | 49. (d)  | 50. (c)  |
| 51. (a)  | 52. (d)  | 53. (a)  | 54. (b)  | 55. (d)  | 56. (b)  | 57. (c)  | 58. (d)  | 59. (b)  | 60. (d)  |
| 61. (a)  | 62. (b)  | 63. (b)  | 64. (b)  | 65. (c)  | 66. (c)  | 67. (b)  | 68. (c)  | 69. (c)  | 70. (a)  |
| 71. (d)  | 72. (d)  | 73. (a)  | 74. (a)  | 75. (c)  | 76. (d)  | 77. (a)  | 78. (c)  | 79. (d)  | 80. (d)  |
| 81. (c)  | 82. (d)  | 83. (a)  | 84. (d)  | 85. (b)  | 86. (b)  | 87. (c)  | 88. (a)  | 89. (c)  | 90. (d)  |
| 91. (b)  | 92. (a)  | 93. (b)  | 94. (a)  | 95. (a)  | 96. (b)  | 97. (d)  | 98. (c)  | 99. (a)  | 100. (d) |
| 101. (c) | 102. (a) | 103. (c) | 104. (d) | 105. (c) | 106. (b) | 107. (a) | 108. (d) | 109. (a) | 110. (b) |
| 111. (b) | 112. (b) | 113. (c) | 114. (a) | 115. (d) | 116. (b) | 117. (a) | 118. (c) | 119. (d) | 120. (a) |
| 121. (b) | 122. (d) | 123. (c) | 124. (d) | 125. (c) |          |          |          |          |          |

### One or More Than One Options Correct

1. (a,b,c)    2. (a,b,c)    3. (a,b,c)    4. (a,b,c,d)
5. (a,b,c)    6. (a,b)    7. (a,b,c,d)    8. (a,c)    9. (a)
10. (a,b)

### Passage Comprehension Questions

#### Passage 1

1. (d)    2. (b,d)    3. (b)    4. (b)    5. (a)    6. (d)

#### Passage 2

1. (c)

#### Passage 3

1. (a,c)    2. (d)

#### Passage 4

1. (b)    2. (c)
3. (d)

$$\text{pH} = 7 + \frac{\text{p}K_a}{2} + \frac{\log C}{2}$$

$$= 7 + \frac{2x}{2} - 1 = (6 + x)$$

#### Passage 5

1. (a)    2. (d)

#### Passage 6

1. (b)    2. (a)    3. (c)

#### Passage 7

1. (c)    2. (d)    3. (c)    4. (a)



## Set I

# 14

## Group 16 (VIA—The Chalcogens)

**"I am king" of acids. I can dehydrate every thing even skin. I can cause boiling of water with violent splashing of added into my concentrated form" Guess me.**

Oxygen is the most abundant element in the earth's crust, representing slightly less than 50% of it by weight. It is present as elemental oxygen in the atmosphere and is combined with other elements in water and in many minerals. Sulphur, seventeenth in abundance in the earth's crust occurs as sulphide (HgS, PbS etc) in natural gas and oil, as disulphide ion ( $\text{FeS}_2$ —"fools' gold") as sulphate ( $\text{CaSO}_4$ )

Selenium and tellurium are comparatively rare on earth's crust, having abundance as selenide/telluride of Cu, Ag, Fe, As.

### Periodicity in Group 16 (VIA—The Chalcogens)

- The first four elements are called chalcogens meaning ore forming (oxides, sulphides, selenides, tellurides).
- Some representative properties of group 16 (VI A) elements are given in Table 14.1 and Fig. 14.1.

Similar to the groups discussed earlier, the metallic character in group 16 increases with increasing atomic number. Oxygen and sulphur are entirely non-metallic in their chemical behaviour. Selenium and tellurium, though essentially non-metallic, assume increasing metallic character and are termed as metalloids. Polonium is most metallic in the group.

Density, melting and boiling points covalent and ionic radii, show a regular increase from oxygen to polonium. The large difference in melting and boiling points between oxygen and sulphur can be explained on the basis of their structure. Oxygen exists mostly as a diatomic molecule held together by weak

### Learning Framework of the Chapter

- Periodicity in Group 16  
(VIA—The Chalogens)
- Ozone ( $\text{O}_3$ )
- Allotropy and Polymorphism of Sulphur
- Study of Compounds of Group 16 (VIA)

van der Waals' forces while others exist as polyatomic molecules, e.g.,  $S_8$ ,  $Se_8$ , etc., where the atoms are bonded by covalent bonds associated with high dissociation energy. Their existence as diatomic and polyatomic molecules can be explained as follows: The  $O=O$  bond more than three times as strong as the  $O-O$  bond. By comparison the  $S=S$  bond is less than twice as strong as the  $S-S$  single bond. This results in catenated  $-O-O-O-$  chains beginning unstable relative to  $O=O$ ; but catenated  $-S-S-S-$  chains being stable relative to the molecule  $S=S$ .

| Bond  | Bond energy $\text{kJ mol}^{-1}$ |
|-------|----------------------------------|
| $O=O$ | 498                              |
| $O-O$ | 142                              |
| $S=S$ | 431                              |
| $S-S$ | 265                              |

The elements of group 16 are characterised by high ionisation energies. (Fig 14.1) decreasing gradually from oxygen to polonium. The high values indicate reluctance of these elements to form cations. Their electronegativities decrease with increasing atomic number. This, is

view of the fall in electronegativity, metallic character within the group increases with increasing atomic size.

Oxygen, the second most electronegative element, fluorine being the first, has a strong tendency to accept two electrons and give  $O^{2-}$  ion. Thus, almost all metal oxide are ionic and contain  $O^{2-}$  ions.

### DEEP Focus

Usually oxygen exhibits as oxidation state  $-2$  in its other compounds also. It exhibits positive oxidation state only in a few compounds formed with fluorine, i.e.,  $OF_2$  and  $O_2F_2$ . The tendency for the formation of divalent anions decreases from sulphur downwards because of the increasing size and decreasing electronegativity of the elements. Sulphur, selenium and tellurium show a tendency for covalency with formal oxidation states  $+2$ ,  $+4$  and  $+6$  in compounds in which they are combined with more electronegative elements such as oxygen and halogens. In the higher oxidation state of  $+4$  and  $+6$  of these elements electrons are unpaired and promoted to vacant  $d$ -orbitals.

Table 14.1 Physical Properties of the Element in Group 16 (VIA)

|                                                         | $O_8$            | $S_{16}$         | $Se_{34}$                | $Te_{52}$                | $Po_{84}$                        |
|---------------------------------------------------------|------------------|------------------|--------------------------|--------------------------|----------------------------------|
| Electronic configuration                                | $[He] 2s^2 2p^4$ | $[Ne] 3s^2 3p^4$ | $[Ar] 3d^{10} 4s^2 4p^4$ | $[Kr] 4d^{10} 5s^2 5p^4$ | $[Xe] 4f^{14} 5d^{10} 6s^2 6p^4$ |
| Covalent radius (pm)                                    | 74               | 104              | 114                      | 137                      | 168                              |
| Ionic radius ( $M^{2-}$ , pm)                           | 140              | 184              | 198                      | 221                      | —                                |
| $(IE)_1/\text{kJ mol}^{-1}$                             | 1314             | 999              | 941                      | 869                      | 813                              |
| Electronegativity                                       | 3.5              | 2.5              | 2.4                      | 2.1                      | 2.0                              |
| Melting point ( $^{\circ}\text{C}$ )                    | $-229$           | $114^*$          | $221^a$                  | 452                      | 254                              |
| Boiling point ( $^{\circ}\text{C}$ )                    | $-183$           | 445              | 685                      | 1087                     | 962                              |
| Density ( $10^3 \times \text{kg m}^{-3}$ )              | 1.14             | 2.07             | 4.79                     | 6.25                     | 9.4                              |
| Oxidation states                                        | $-2, -1, +1, +2$ | $-2, +2, +4, +6$ | $-2, +2, +4, +6$         | $-2, +2, +4, +6$         | $+2, +4$                         |
| Electron affinity ( $\text{kJ mol}^{-1}$ )              | $-141$           | $-200$           | $-195$                   | $-190$                   | $-183$                           |
| $E^{\circ}/V$ for<br>$X + 2H^+ + 2e^- \rightarrow H_2X$ | 1.23             | 0.14             | $-0.40$                  | $-0.79$                  | —                                |

\*Rhombic sulphur,  $\alpha$ -Grey Se

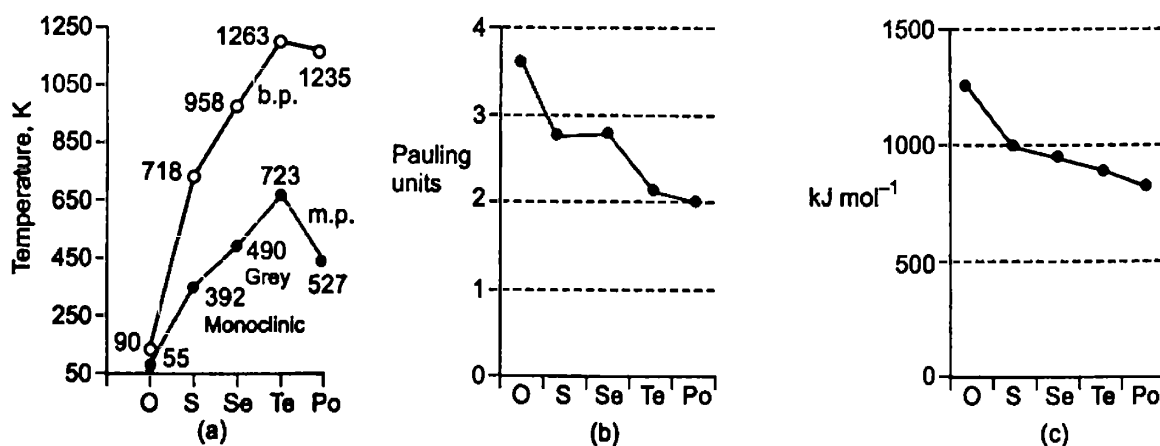


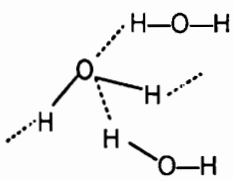
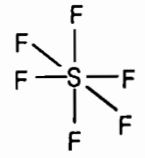
Fig. 14.1 Some group trends of the group 16 elements : (a) Boiling point and melting point, (b) Pauling electronegativity, and (c) The first ionisation energy

### DEEP Focus

- One of the points about oxygen is that as the first member of a group it differs in some important ways from other group members due to:
  - small size,
  - high electronegativity, and
  - non-availability of *d*-orbitals for bonding.

Table 14.2 summarises similarities and differences between oxygen and sulphur.

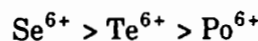
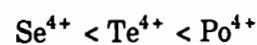
Table 14.2 Comparison of Oxygen and Sulphur

| Oxygen                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | Sulphur                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"> <li>Exists as <math>O_2(g)</math> at 298 K and 1 atm</li> <li>Two allotropes, <math>O_2(g)</math> and <math>O_3(g)</math></li> <li><math>O_2(g)</math> and <math>O_3(g)</math> are very good oxidising agents.</li> <li>Metallic oxides are generally ionic.</li> <li><math>O_2</math> paramagnetic</li> <li>Can form only two and three atom chains as in <math>H_2O_2</math> and <math>O_3</math>. Compounds with O—O bonds decompose readily.</li> <li>Maximum coordination number of oxygen is four, as in water :</li> </ul> | <ul style="list-style-type: none"> <li>Exist as <math>S_8(s)</math> rings at 298 K and 1 atm. At higher temperature <math>S_2</math> predominates.</li> <li>Two solid polymorphic forms and many different molecular species in liquid and gaseous states.</li> <li>S(s) is a poor oxidising agent.</li> <li>Metallic sulphides are ionic (<math>Na_2S</math>, <math>K_2S</math>...) as well as covalent insoluble in water (<math>CuS</math>, <math>NiS</math>, <math>CdS</math>... generally of <i>d</i>-block)</li> <li><math>S_2</math> paramagnetic</li> <li>Can form molecules with up to six S atoms per chain in compounds such as <math>H_2S_n</math>, <math>Na_2S_n</math>, <math>H_2S_nO_6</math>.</li> <li>Maximum coordination number of sulphur is six, as in <math>SF_6</math> :</li> </ul> |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
| <ul style="list-style-type: none"> <li><math>H_2O</math>:               <ul style="list-style-type: none"> <li>is a liquid at 298 K and 1 atm</li> <li>is extensively hydrogen bonded</li> <li>has a large dipole moment</li> <li>is a good solvent</li> <li>is oxidised with difficulty</li> <li>forms hydrated and aqua complexes.</li> </ul> </li> </ul>                                                                                                                                                                                                          | <ul style="list-style-type: none"> <li><math>H_2S</math> <ul style="list-style-type: none"> <li>is a (poisonous) gas at 298 K and 1 atm</li> <li>is not hydrogen bonded</li> <li>has a small dipole moment</li> <li>is a poor solvent</li> <li>forms no complexes</li> <li>is easily oxidised.</li> </ul> </li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |

- Selenium has unique property of photoconductivity and is used in photocopying (xerox) machines and also a decoloriser of glass. Te and Po are highly toxic, Po is higher due to its intense radioactivity. Se and Te are found as selenides and tellurides in sulphide ores ( $Cu_2Se$ ,  $Cu_2Te$ ). **The colour of the red glass in the traffic signals is due to  $CdSe$ .**

### Oxidation States

- With valence electronic configuration  $ns^2np^4$ , the group 16 (VI A) elements are just two electron short of an octet configuration, and  $-2$  oxidation state is therefore, a common one. The stability of  $-2$  state decreases with increasing metallic character as indicated by  $E^\circ$  (redox) values. Oxygen is powerful oxidising agent and  $H_2Se$  and  $H_2Te$  are reducing agents ( $E^\circ$  values of Se and Te are negative). Because S, Se, and Te are much less electronegative than oxygen, they are commonly found in positive oxidation states as  $+4$  in  $SF_4$ ,  $SO_2$  and  $H_2SO_3$  and  $+6$  in  $SF_6$ ,  $SO_3$ ,  $H_2SO_4$ .
- Unlike oxygen, the maximum coordination number of sulphur and other elements can exceed **four** and valency is not limited to **two** because of available *d*-orbitals for bonding. Stability of  $+6$  state decreases and that of  $+4$  state increases going down the group due to inert-pair effect. It is:

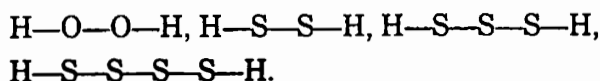


### Hydrides

- $H_2Se$  and  $H_2Te$  are unpleasant gaseous hydrides like  $H_2S$  but less stable than  $H_2S$ , order of thermal stability being  $H_2O > H_2S > H_2Se > H_2Te > H_2Po$ .
- Oxyacids of S, Se and Te exist and  $H_2SO_4$  and  $H_2SeO_4$  are considered as strong acids.

### Catenation

- The tendency for catenation decreases markedly as we go down the group. This property is prominently displayed by sulphur ( $S_8$ ). The S—S bond is important in biological systems and is found in compounds such as cysteine, some proteins and enzymes. Stable polyoxides and polysulphides are known. Examples are:



### Metallic Nature

- The metallic character increases as we descend the group. S is non-metal and insulator. Se and Te are metalloids and are semiconductors. Po is a metal.

### Multiple Bonding

- The tendency to form multiple bonds to C, N and O decreases as we descend the group from Se to Te. Thus  $S=C=S$  is moderately stable;  $Se=C=Se$  decomposes readily whereas  $Te=C=Te$  does not exist.
- Acidic nature of hydride increases as we go down the group:



## Halides

- The form halides of different oxidation number +1, +2, +4 and +6.

| Halides                             | X            | Oxidation numbers |
|-------------------------------------|--------------|-------------------|
| S <sub>2</sub> X <sub>2</sub>       | F, Cl, Br, I | +1                |
| SX <sub>2</sub>                     | F, Cl        | +2                |
| SX <sub>4</sub>                     | F            | +4                |
| SX <sub>6</sub>                     | F            | +6                |
| Se <sub>2</sub> X <sub>2</sub>      | Cl, Br       | +1                |
| SeX <sub>2</sub> , TeX <sub>2</sub> | Cl, Br       | +2                |
| SeX <sub>4</sub> , TeX <sub>4</sub> | F, Cl, Br    | +4                |
| TeX <sub>4</sub>                    | I            | +4                |
| SeX <sub>6</sub> , TeX <sub>6</sub> | F            | +6                |

The stability of the halides decreases in the order  $F > Cl > Br > I$ . +6 oxidation is observed in fluoride, while iodide of Te (TeI<sub>4</sub>) is formed.

SF<sub>6</sub> is thermodynamically inert, non-toxic gas. Inertness of SF<sub>6</sub> is due to the presence of sterically protected sulphur atom. SF<sub>6</sub> is used as a gaseous insulator in high voltage generators. SF<sub>4</sub> and SeF<sub>4</sub> are good fluorinating agents and —COOH group can be converted into CF<sub>3</sub> and  $>C=O$  and —P=O into CF<sub>2</sub> and —PF<sub>2</sub> groups.

- Oxides of sulphur are more stable than the corresponding oxides of other elements.

## Reactions

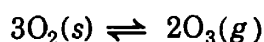
Reactions of the group 16 (VIA) elements are summarised below:

| General equations                                                           | Remarks                                                               |
|-----------------------------------------------------------------------------|-----------------------------------------------------------------------|
| $x\text{E} + y\text{M} \longrightarrow \text{M}_y\text{E}_x$                | With many metals                                                      |
| $z\text{E} + \text{M}_x\text{E}_y \longrightarrow \text{M}_x\text{E}_{y+z}$ | Especially with S and Se                                              |
| $\text{E} + \text{H}_2 \longrightarrow \text{H}_2\text{E}$                  | Decreasing in the series O <sub>2</sub> , S, Se, Te                   |
| $\text{E} + 3\text{F}_2 \longrightarrow \text{EF}_6$                        | With S, Se, Te and excess F <sub>2</sub>                              |
| $2\text{E} + \text{Cl}_2 \longrightarrow \text{E}_2\text{Cl}_2$             | With S, Se (Te gives TeCl <sub>2</sub> ); also with Br <sub>2</sub>   |
| $\text{E}_2\text{Cl}_2 + \text{Cl}_2 \longrightarrow 2\text{ECl}_2$         | With S, Se, also with Br <sub>2</sub>                                 |
| $\text{E} + 2\text{Cl}_2 \longrightarrow \text{ECl}_4$                      | With S, Se, Te and excess Cl <sub>2</sub> ; also with Br <sub>2</sub> |
| $\text{E} + \text{O}_2 \longrightarrow \text{EO}_2$                         | With S (with Se, use O <sub>2</sub> and NO <sub>2</sub> )             |

(E = O, S, Se, Te, Po and M metal).

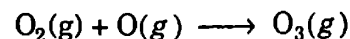
## Ozone (O<sub>3</sub>)

- In the laboratory, O<sub>3</sub> can be made by passing oxygen through a strong electric field. An equilibrium is set up:



It is only a metastable allotrope, always having a tendency to convert back into oxygen.

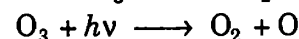
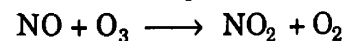
- Some 30 km above the earth's surface oxygen molecules can be split apart by UV light from the sun. Some of the atoms join with other oxygen molecules to make ozone:



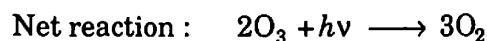
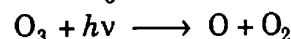
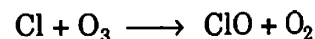
- O<sub>3</sub> is an unstable, dark blue diamagnetic gas, boiling point –112°C. The colour is due to intense absorption of red light. It also absorbs strongly in the UV region. This is particularly important since there is a layer of O<sub>3</sub> in the upper atmosphere which absorbs harmful UV radiation from the sun, thus protecting people on the earth. The use of chlorofluorocarbons (CFC) in aerosols and refrigerators, and their subsequent escape into the atmosphere, is blamed for making holes in the ozone layer over the Antarctic and Arctic. It is feared that this will allow an excessive amount of UV light to reach the earth which will cause melanoma (skin cancer) in humans. Oxides of nitrogen (from car exhausts) and the halogens can also damage the O<sub>3</sub> layer.

### Ozone destroying reactions:

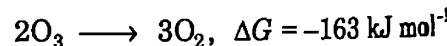
— based on oxides of nitrogen



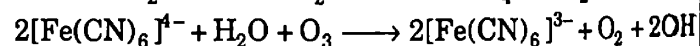
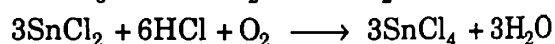
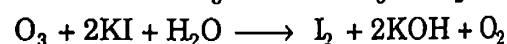
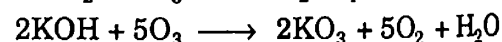
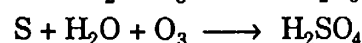
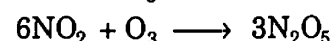
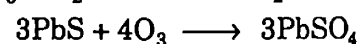
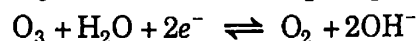
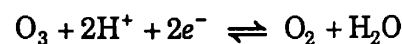
— based on reactive chlorine species from CFC



- O<sub>3</sub> is thermodynamically unstable, and decomposes to O<sub>2</sub>:



- O<sub>3</sub> is an extremely powerful oxidising agent:

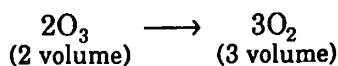


- Potassium ozonide KO<sub>3</sub> is an orange coloured solid and contains the paramagnetic O<sub>3</sub><sup>–</sup> ion.

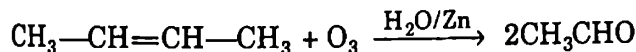
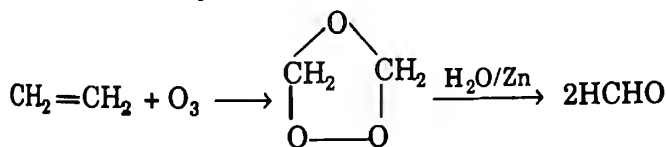
## DEEP Focus

- The amount of O<sub>3</sub> in a gas mixture can be determined by passing the gas into a KI solution (at a constant pH 9.5 using borate buffer). The iodine that is liberated is titrated with sodium thiosulphate solution

- $O_3$  can also be decomposed catalytically and change in volume measured :

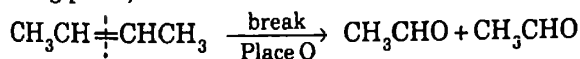


- $O_3$  also adds to unsaturated organic compounds at room temperature forming ozonides which can be cleaved to aldehydes and ketones in solution :

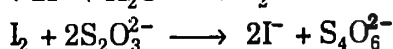
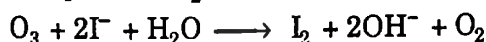


### DEEP Focus

To derive products of ozonolysis, break (C=C) bond, place O at breaking point,

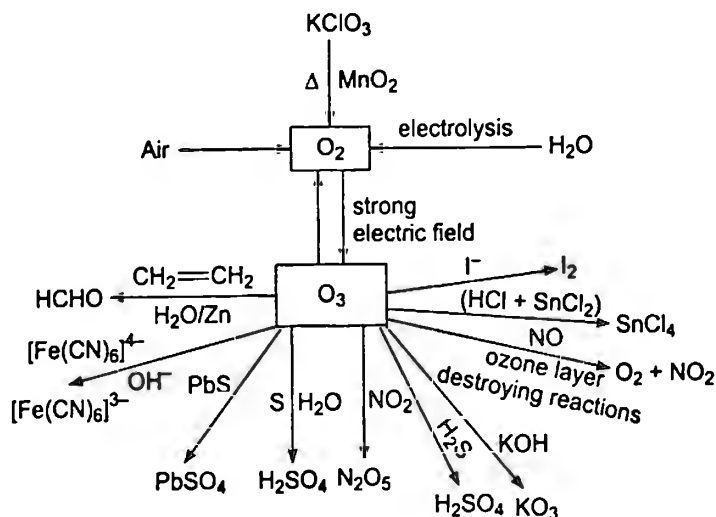


- $O_3$  is used as a disinfectant; it is used to purify drinking water since, it can destroy bacteria and viruses. It is better than  $Cl_2$  since, it ( $O_3$ ) avoids the unpleasant smell and taste of  $Cl_2$  and any excess  $O_3$  soon decomposes to  $O_2$ .

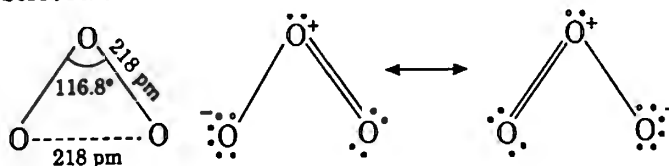


$$O_3 \equiv I_2 \equiv 2I \equiv 2S_2O_3^{2-}$$

∴ Equivalent weight of  $O_3 = \frac{\text{molecular weight}}{2}$



The molecules  $O_3$  is bent with an O—O—O angle  $116.8^\circ$  and equal O—O distance of 128 pm and may be described  $90^\circ$  canonical forms.

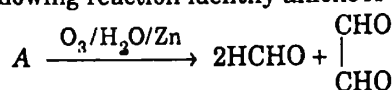


## Target Practice 1

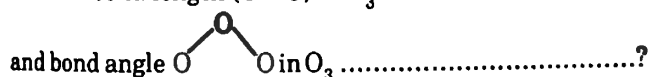
1. Write the formulae of the compounds with given oxidation number of the given elements.

|     | Element | O.N. | Compounds |
|-----|---------|------|-----------|
| (a) | O       | +2   | .....     |
| (b) | O       | -1   | .....     |
| (c) | O       | -0.5 | .....     |
| (d) | S       | -2   | .....     |
| (e) | S       | +4   | .....     |
| (f) | S       | +6   | .....     |

2. Based on following reaction identify alkene A



3. What is bond length (O—O) in  $O_3$  .....



4.  $2O_3 \longrightarrow 3O_2$ ;  $\Delta G^\circ = -163 \text{ kJ mol}^{-1}$   
Is this reaction spontaneous. Yes/No .....

5. Write reaction representing  $O_3$  as an oxidising agent

(a) in acidic medium .....

(b) in basic medium .....

Equivalent weight in (a) .....

Equivalent weight in (b) .....

6. Compare oxygen and fluorine in following properties

|                                       |          |                      |       |
|---------------------------------------|----------|----------------------|-------|
| (a) Electronegativity                 | O        | <input type="text"/> | F     |
| (b) Electron affinity                 | O        | <input type="text"/> | F     |
| (c) Reactivity                        | $O_2$    | <input type="text"/> | $F_2$ |
| (d) Bond energy to form gaseous atoms | $O_2$    | <input type="text"/> | $F_2$ |
| (e) Covalent radius                   | O        | <input type="text"/> | F     |
| (f) Ionic radius                      | $O^{2-}$ | <input type="text"/> | $F^-$ |

## Answers

1. (a)  $OF_2$  (b)  $H_2O_2$  (c)  $KO_2$  (d)  $H_2S$  (e)  $SO_2$  (f)  $SO_3$

2.  $CH_2=CH-CH=CH_2$

3. Bond length = 128 pm, Bond-angle =  $116.8^\circ$

4. Yes (since  $\Delta G^\circ < 0$ )

5. (a)  $O_3 + 2H^+ + 2e^- \rightleftharpoons O_2 + H_2O$

- (b)  $O_3 + H_2O + 2e^- \rightleftharpoons O_2 + 2OH^-$

$$\text{Equivalent weight in (a)} = \frac{48}{2} = 24 \text{ g equivalent}^{-1}$$

$$\text{Equivalent weight in (b)} = \frac{48}{2} = 24 \text{ g equivalent}^{-1}$$

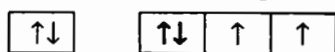
6. (a)  $O < F$  (b)  $O < F$  (c)  $O_2 > F_2$  (d)  $O_2 > F_2$  (e)  $O > F$   
(f)  $O^{2-} > F^-$

## Practice Exercise 1

- Explain.
  - $O_2$  is paramagnetic
  - $H_2O$  is liquid while  $H_2S$  is gas under given conditions
  - Boiling point of  $H_2O$  is abnormally high
- What is coordination number of oxygen in  $H_2O(l)$ ?
- From the trend of  $(IE)_1$  as in Table 14.1, what do you conclude about the nature of polonium?
- Polonium also exhibits +2 oxidation state, explain.
- Identify the group 16 (VI A) element that fits each of the following description in:
  - the most electronegative
  - a semimetal
  - radioactive
  - the most abundant element in the earth's crust.
- $O_3$  is diamagnetic and O to O bond lengths are equal. Explain.
- $O_3$  is a powerful oxidising agent. Write equations to represent oxidation of
  - $I^-$  to  $I_2$  in acidic solutions,
  - sulphur to sulphuric acid in the presence of moisture,
  - $[Fe(CN)_6]^{4-}$  to  $[Fe(CN)_6]^{3-}$  in basic solution.
- It has been estimated that if all the  $O_3$  in the atmosphere were brought to sea level at STP, the gas would form a layer 0.3 cm thick. Estimate the number of  $O_3$  molecules in the earth's atmosphere.  
(radius of the earth is 4000 mile, 1 km = 0.6214 mile)
- Alkene ( $C_6H_{12}$ )  $\xrightarrow[Zn]{O_3/H_2O}$   $2CH_3COCH_3$   
Identify alkene.

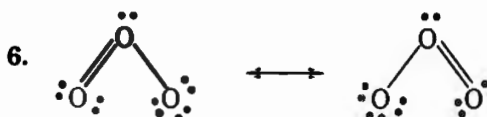
## Answers

- (a) It is due to presence of two unpaired electrons in anti-bonding molecular orbitals  
 $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_x)^2(\pi 2p_y)^2(\pi 2p_z)^2(\pi^* 2p_y)^1(\pi^* 2p_z)^1$
- $H_2O$  molecules have intermolecular H-bonding due to greater electronegativity of oxygen hence,  $H_2O$  is liquid;  $H_2S$  lacks H-bonding hence, gas.
- Due to intermolecular H-bonding.
- Four.
3. It is least, hence metallic.
- It is due to inert-pair effect of  $ns$ -pair as well as  $np$ -pair



(both are inert due to shielding effect hence difficult to unpair—hence +2 oxidation state)

- (a) O (b) Te (c) Po (d) O

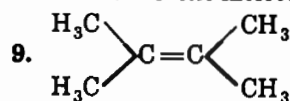


Due to resonance, two O—O bonds are equivalent and have a bond order of 1.5 (bond length = 128 pm, angle =  $116.5^\circ$ )

All electrons appear paired hence diamagnetic.

- $O_3 + 2I^- + 2H^+ \longrightarrow O_2 + I_2 + H_2O$
  - $3O_3 + S + H_2O \longrightarrow H_2SO_4 + 3O_2$
  - $O_3 + 2[Fe(CN)_4]^{4-} + H_2O \longrightarrow 2[Fe(CN)_6]^{3-} + 2OH^- + O_2$

- $4 \times 10^{37}$  ozone molecules.



## Allotropy and Polymorphism of Sulphur

Many different molecular species are possible for the elemental sulphur, and this accounts for the existence of the large number of physical forms in which the element may appear as shown in Fig. 14.2. Allotropy is more complex for the element sulphur than for any other element of group 16(VI). Sulphur may exist as:

- rhombic sulphur ( $S_\alpha$ )** which has sixteen  $S_8$  rings in a unit cell and at  $95.5^\circ\text{C}$  converts to:
- monoclinic sulphur ( $S_\beta$ )** which has six  $S_8$  rings in its unit cell. It melts at  $119^\circ\text{C}$ , yielding:
- liquid sulphur ( $S_\lambda$ )** comprised of  $S_8$  molecules. This is yellow, transparent, mobile liquid. At  $160^\circ\text{C}$ , a remarkable transformation occurs. The  $S_8$  rings open

up and join together into long spiral-chain molecules, resulting in:

- liquid sulphur ( $S_\mu$ )**

which is a dark in colour and very thick and viscous. The chain length and viscosity of the liquid reach a maximum at about  $180^\circ\text{C}$ . At higher temperatures the chains break up and viscosity decreases again. At  $445^\circ\text{C}$ , this liquid boils, producing:

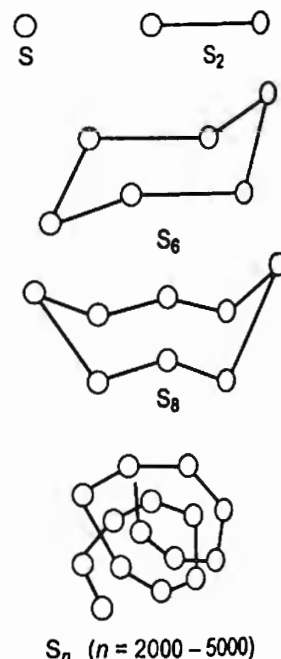
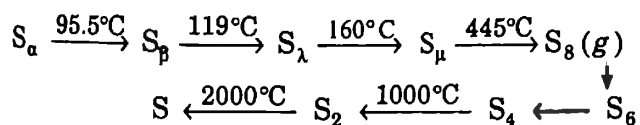


Fig. 14.2 Different molecular forms of sulphur

- **Sulphur vapours**, which consists of molecules ranging from  $S_2$  to  $S_{10}$ , but predominantly  $S_8$ . At higher temperatures,  $S_2$  predominates.  $S_2$  is paramagnetic.

- Plastic sulphur forms if liquid sulphur ( $\mu$ ) is poured into cold water. It consists of chain-like molecules and has rubber-like properties when first formed. On standing, it becomes brittle and finally converts to rhombic sulphur.

Above transformations can be written as:



- If rhombic sulphur is heated rapidly, it fails to convert into monoclinic sulphur and melts at  $113^\circ\text{C}$ .
- In  $\text{cyclo-}S_6$ , the ring adopts the chain form chain polymers, **catena- $S_n$**  are also known.

## Production of Sulphur

### Frasch Process

Sulphur occurs abundantly in the earth's crust as elemental sulphur, as mineral sulphides and sulphates, as  $H_2S$  in natural gas, and as organic sulphur compounds in oil and coal. The sulphur is mined in an unusual way, known on the **Frasch process** (Fig. 14.3).

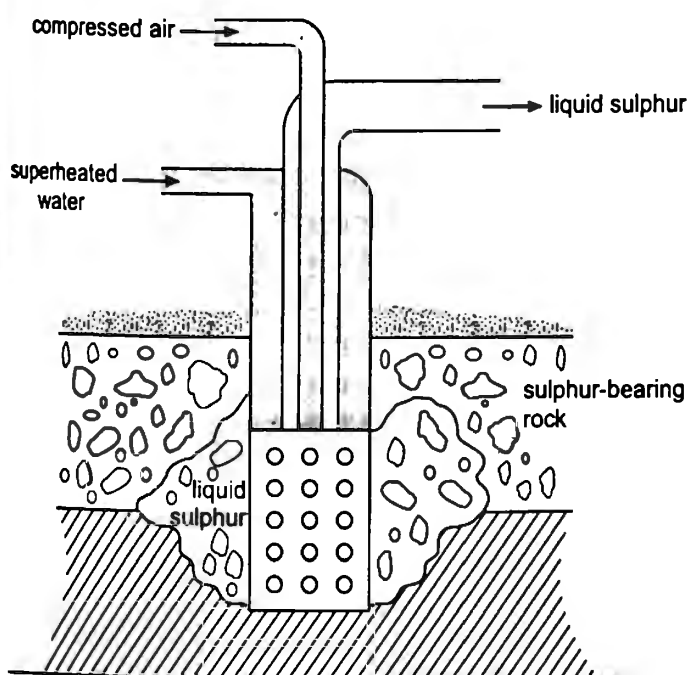


Fig. 14.3 Frasch process for production of sulphur

A mixture of superheated water and steam (at about  $160^\circ\text{C}$  and 16 atm) is forced down the outermost of three concentric pipes into an underground bed of sulphur containing rock. The sulphur melts and forms a liquid pool. Compressed air (at 20–25 atm) is pumped down the innermost pipe and forces liquid sulphur up the remaining pipe. The liquid sulphur is either stored and shipped as a

liquid (by tank car, ship, or pipeline) or allowed to solidify to a solid.

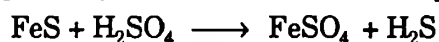
Although the Frasch process was once the principal source of elemental sulphur this is no longer the case. The change has been brought, about by the need to control sulphur emissions from industrial operations. In one process to remove  $H_2S$  from a gaseous mixture, the gas stream is split into two parts. One part (consisting of about one-third of the stream) is burnt to convert  $H_2S$  to  $SO_2$ . The streams are rejoined in a catalytic converter at 200 to  $300^\circ\text{C}$ , where this reaction occurs.



## Study of Compounds of Group 16 (VIA)

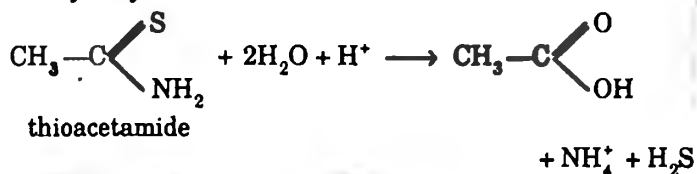
### Hydrides ( $H_2S$ )

- All form **covalent** hydrides. Water ( $H_2O$ ) is liquid at room temperature but others are all colourless, foul smelling toxic gases.
- A comparative study of hydrides of this group are given in Table 14.3.
- $H_2S$  is prepared by reaction of  $FeS$  on dil.  $H_2SO_4$ :



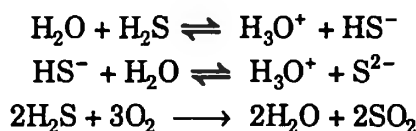
### DEEP Focus

- Now a days,  $H_2S$  used in qualitative analysis is prepared by the hydrolysis of thioacetamide:



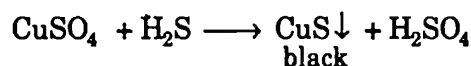
Use of thioacetamide is useful as it produces  $H_2S$  *in situ*, and thus causes no pollution.

- $H_2S$  is soluble in water and burns in air with a blue flame :

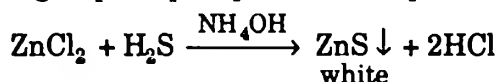


- A saturated solution of  $H_2S$  is used as a laboratory reagent for qualitative analysis of basic radicals (cations) :

– in acidic medium ( $HCl$ ),  $Cu^{2+}$ ,  $Pb^{2+}$  ..... of II group are precipitated as sulphides



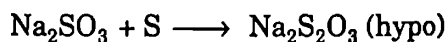
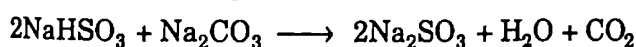
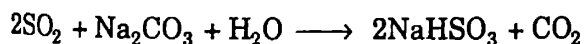
– in basic (ammoniacal) medium,  $Zn^{2+}$ ,  $Ni^{2+}$  ..... of IV group are precipitated as sulphides :





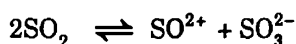


- $\text{SO}_2$  is used to make other products :

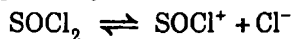


### DEEP Focus

- Liquid  $\text{SO}_2$  has also been used as a non-aqueous solvent and is a useful reaction medium for organic and inorganic compounds :



Radioactive isotopic study shows that  $\text{SOCl}_2$  ionises as

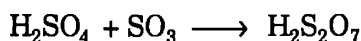


and not as  $\text{SOCl}_2 \rightleftharpoons \text{SO}^{2+} + 2\text{Cl}^-$

Thus, formation of  $\text{SO}^{2+}$  in liquid  $\text{SO}_2$  is not favourable.

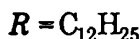
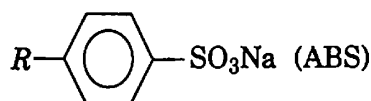
- The  $\text{SO}_3$  is not usually isolated, and practically all of it is converted to  $\text{H}_2\text{SO}_4$ .

- $\text{H}_2\text{SO}_4$  saturated with  $\text{SO}_3$  is called **oleum** (pyrosulphuric acid)



### DEEP Focus

- $\text{SO}_3$  is used for the sulphonation of long chain alkyl benzene compounds (like dodecyl benzene). The sodium salt of these alkyl benzene sulphonic acid are anionic surface-active agents, and are the active ingredients of detergents :



ABS (Alkyl Benzene Sulphonates)

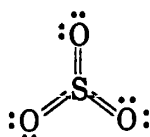
- $\text{SO}_3 + \text{H}_2\text{SO}_4 + \text{NH}_2\text{CONH}_2 \longrightarrow 2\text{NH}_2\text{SO}_3\text{H} + \text{CO}_2$   
sulphamic acid

## Structure

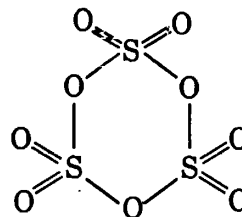
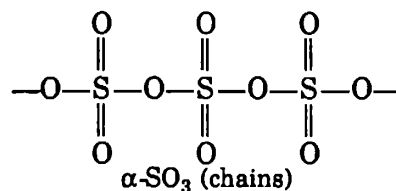
- $\text{SO}_2$  gas forms discrete V-shaped molecule and this structure is retained in solid state.
- The sulphur atom is  $sp^2$  hybridised but bond angle  $\angle\text{OSO}$  is  $119^\circ 30'$ . It is due to VSEPR (valence shell electron pair repulsion) :



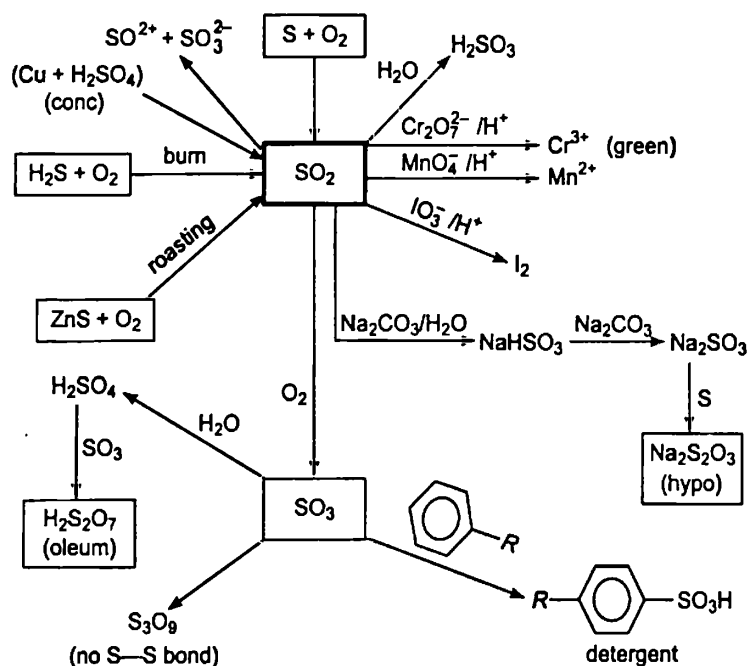
- In the gas phase  $\text{SO}_3$  has a plane triangular structure. The bonding is best described as S forming three  $\sigma$  bonds, giving rise to plane triangle, and three delocalised  $\pi$ -bonds :



At room temperature,  $\text{SO}_3$  is solid and exists as :



$\gamma\text{-SO}_3$  (cyclic, ice-like)

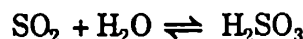


## Oxoacids of Sulphur

- The oxoacids of sulphur are more numerous and are summarised in Table 14.4.
- Acids ending in **-ous** have S in the **oxidation state (+IV)**, and form salts ending in **-ite**. Acids ending in **-ic** have S in the **oxidation state (+VI)** and form salt ending in **-ate**.
- In peroxy acids, there is a peroxy linkage (with oxidation number of each oxygen in peroxide -1) hence oxidation number of sulphur is (+VI).
- In  $\text{H}_2\text{S}_2\text{O}_3$  one sulphur is attached to central S, hence, its oxidation state is (-II) as in oxygen.
- $\text{H}_2\text{SO}_4$  (oxidation number of S = VI) is stronger than  $\text{H}_2\text{SO}_3$  (oxidation number of S = IV).

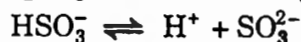
## Sulphurous Acid ( $\text{H}_2\text{SO}_3$ )

- The acid is obtained by dissolving  $\text{SO}_2$  gas in  $\text{H}_2\text{O}$  :

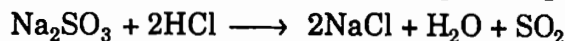
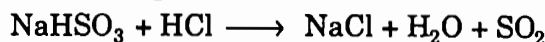


It actually exists as  $\text{SO}_2 \cdot \text{H}_2\text{O}$  and this acid is known only in solution.

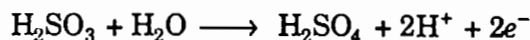
- A strong diprotic acid:



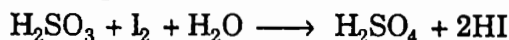
$\text{NaHSO}_3$  is thus an acid salt and  $\text{Na}_2\text{SO}_3$  is normal salt and both liberate  $\text{SO}_2$  gas on reaction with acid:



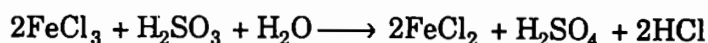
- The acid is a good **reducing agent**:



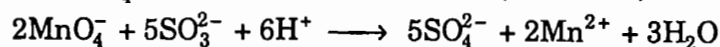
–  $\text{X}_2(\text{Cl}_2, \text{Br}_2, \text{I}_2)$  is reduced to  $\text{HX}$



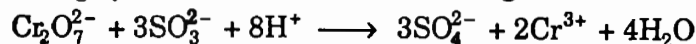
–  $\text{Fe}^{3+}$  salts are reduced to  $\text{Fe}^{2+}$  salts



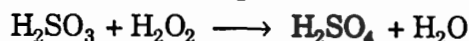
–  $\text{MnO}_4^-$  (violet) is reduced to  $\text{Mn}^{2+}$  (colourless)



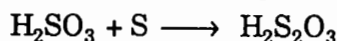
–  $\text{Cr}_2\text{O}_7^{2-}$  (orange) is reduced to  $\text{Cr}^{3+}$  (green)



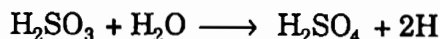
–  $\text{H}_2\text{O}_2$  is reduced to  $\text{H}_2\text{O}$



– It combines with S forming thiosulphuric acid



- It behaves as a good **bleaching agent** and this action is due to nascent H (reducing action)



## DEEP Focus

### Structure

- The sulphite ion exists in crystal and has a pyramidal structure, with one position occupied by lone pair. S-atom is  $sp^3$  hybridised but bond angle  $\text{O}-\text{S}-\text{O}$  is  $106^\circ$  (slightly distorted due to lone pair) and the bond lengths are  $151\text{\AA}$ . The ( $d\pi-p\pi$ ) bond between S and O is delocalised, and hence, the S—O bonds have a bond order of 1.33

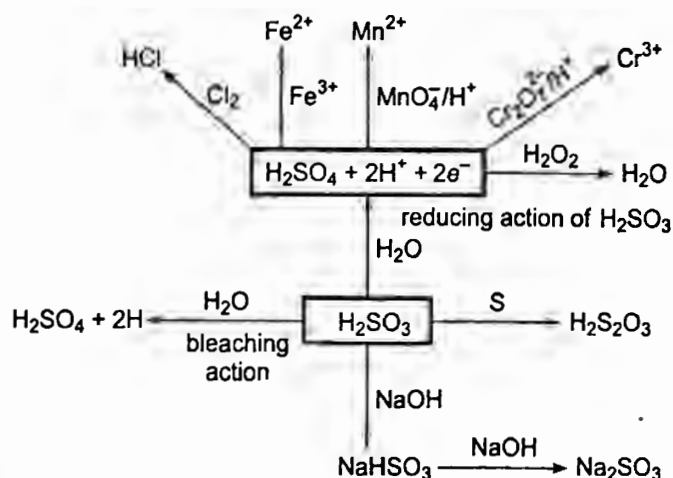
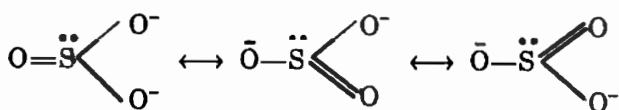


Table 14.4 Oxoacids of Sulphur

### 1. Sulphurous acid series

|                                      |                    |                                             |                                                                         |
|--------------------------------------|--------------------|---------------------------------------------|-------------------------------------------------------------------------|
| (a) $\text{H}_2\text{SO}_3$          | S (IV)             | sulphurous acid                             | $\text{HO}-\text{S}(=\text{O})-\text{HO}$                               |
| (b) $\text{H}_2\text{S}_2\text{O}_5$ | S (+V)<br>S (+III) | disulphurous acid or<br>pyrosulphurous acid | $\text{H}-\text{O}-\text{S}(=\text{O})_2-\text{S}(=\text{O})-\text{OH}$ |
| (c) $\text{H}_2\text{S}_2\text{O}_4$ | S (+III)           | dithionous acid                             | $\text{HO}-\text{S}(=\text{O})-\text{S}(=\text{O})-\text{OH}$           |

### 2. Sulphuric acid series

|                                      |                   |                    |                                                                            |
|--------------------------------------|-------------------|--------------------|----------------------------------------------------------------------------|
| (a) $\text{H}_2\text{SO}_4$          | S (VI)            | sulphuric acid     | $\text{HO}-\text{S}(=\text{O})_2-\text{OH}$                                |
| (b) $\text{H}_2\text{S}_2\text{O}_3$ | S (VI)<br>S (-II) | thiosulphuric acid | $\text{OH}-\text{S}(=\text{O})_2-\text{OH}$                                |
| (c) $\text{H}_2\text{S}_2\text{O}_7$ | S (VI)            | pyrosulphuric acid | $\text{HO}-\text{S}(=\text{O})_2-\text{O}-\text{S}(=\text{O})_2-\text{OH}$ |

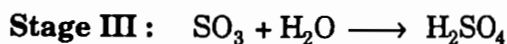
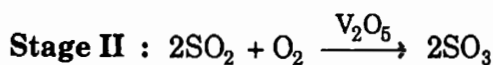
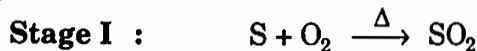
### 3. Peroxo acid series

|                                      |        |                                             |                                                                                     |
|--------------------------------------|--------|---------------------------------------------|-------------------------------------------------------------------------------------|
| (a) $\text{H}_2\text{SO}_5$          | S (VI) | peroxomonosulphuric acid<br>(Caro's acid)   | $\text{HO}-\text{S}(=\text{O})_2-\text{O}-\text{OH}$                                |
| (b) $\text{H}_2\text{S}_2\text{O}_8$ | S (VI) | peroxodisulphuric acid<br>(Marshall's acid) | $\text{HO}-\text{S}(=\text{O})_2-\text{O}-\text{O}-\text{S}(=\text{O})_2-\text{OH}$ |

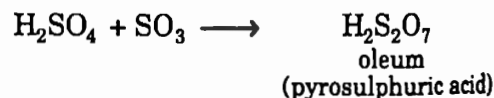
## Sulphuric Acid

- Contact process** (a commercial method)

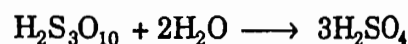
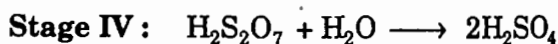
Involves four stages:



This is a violent reaction; instead  $\text{SO}_3$  is passed into 98%  $\text{H}_2\text{SO}_4$

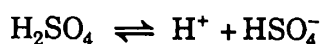


Some trisulphuric acid  $\text{H}_2\text{S}_3\text{O}_{10}$  is also formed.

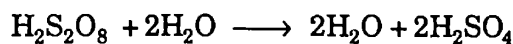
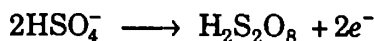




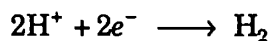
- When conc.  $\text{H}_2\text{SO}_4$  is subjected to electrolysis there is formation of peroxy disulphuric acid and  $\text{H}_2\text{O}_2$  at the anode



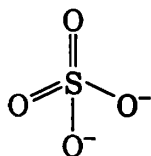
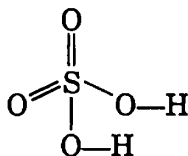
at anode



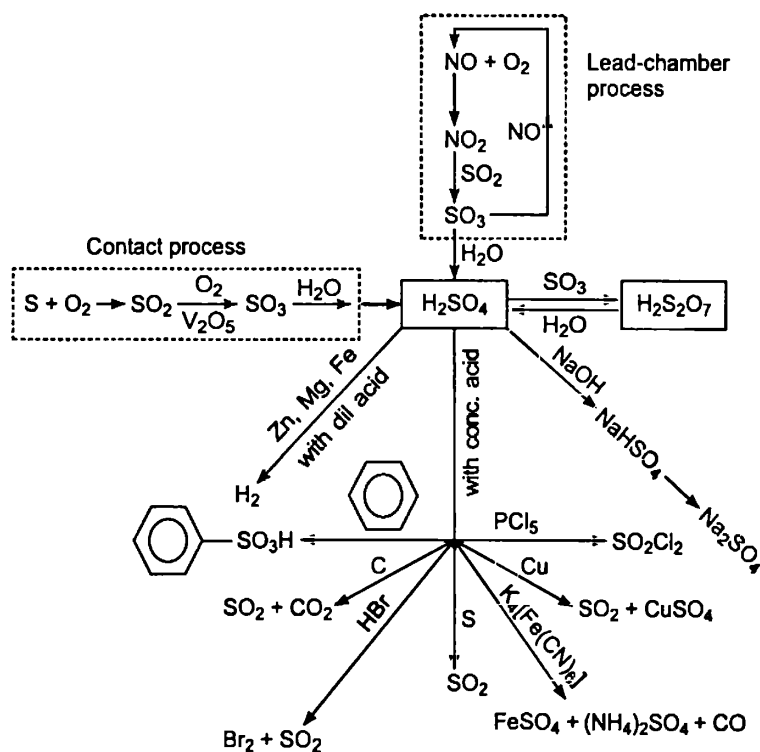
at cathode



## Structure

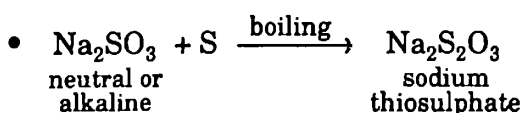


S-atom is  $sp^3$  hybridised.  $\text{SO}_4^{2-}$  ion is tetrahedral. The bond lengths are all equal ( $1.49\text{\AA}$ ) and are all rather short. The bond order of the S—O bonds is approximately 1.5. There are four  $\sigma$ -bonds and two  $\pi$  bonds between S and O atoms (with two  $\pi$ -bonds delocalised over the S and the four O atoms).

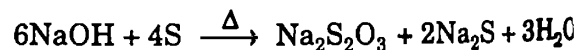
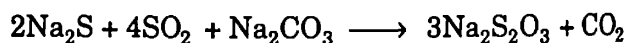
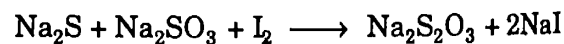


## Sodium Thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ —Hypo)

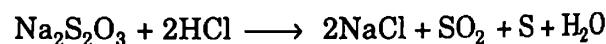
- $\text{H}_2\text{S}_2\text{O}_3$ , thiosulphuric acid, because of its low stability, can't be prepared. However, its salts called thiosulphates can be prepared.



- $2\text{Na}_2\text{S}_3 + 3\text{O}_2 \xrightarrow{\text{heat in air}} 2\text{Na}_2\text{S}_2\text{O}_3 + 2\text{S}$
- Following reactions called **Spring's reactions**, are also used to convert  $\text{Na}_2\text{S}$  or  $\text{S}$  into  $\text{Na}_2\text{S}_2\text{O}_3$ :



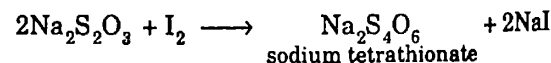
- Hydrated sodium thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , is called '**hypo**'. It forms very large colourless hexagonal crystals, melting point  $48^\circ\text{C}$ .
- It is highly soluble in water.
- It is an efflorescent substance and at  $215^\circ\text{C}$ , it is completely dehydrated to  $\text{Na}_2\text{S}_2\text{O}_3$ .
- Dilute acids like  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  decompose it into  $\text{SO}_2$  and colloidal sulphur (yellowish-white turbidity):



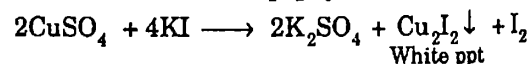
This is a disproportionation reaction.

## DEEP Focus

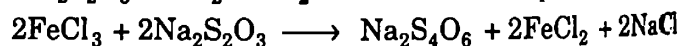
- $\text{I}_2$  oxidises  $\text{Na}_2\text{S}_2\text{O}_3$  into  $\text{Na}_2\text{S}_4\text{O}_6$ :



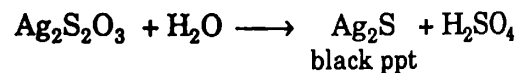
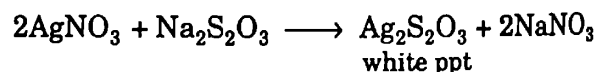
This reaction is used for the iodometric estimation of oxidising agents like  $\text{CuSO}_4$ ,  $\text{CaOCl}_2$ ,  $\text{MnO}_2$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KMnO}_4$  etc., which on reaction with  $\text{KI}$  liberate  $\text{I}_2$  which in turn is determined by titration using  $\text{Na}_2\text{S}_2\text{O}_3$ .



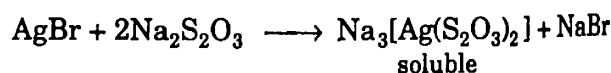
- $\text{Na}_2\text{S}_2\text{O}_3$  is used in the bleaching industry to destroy any excess  $\text{Cl}_2$  on fabrics:



- $\text{AgNO}_3$  reacts with  $\text{Na}_2\text{S}_2\text{O}_3$  giving white ppt changing to yellow, then to brown and finally black:

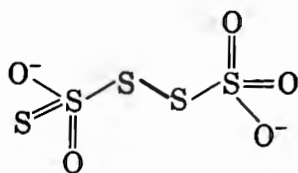
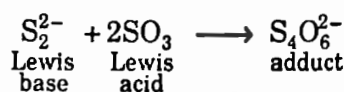


- Hypo is used in photography for '**fixing**' films and prints. It dissolves unreacted  $\text{AgBr}$  from the photographic emulsion by complexation:

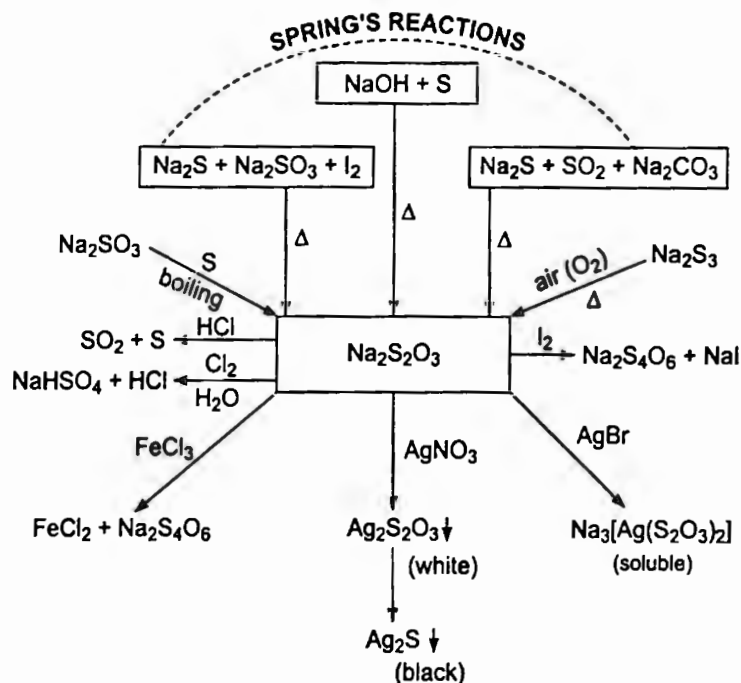
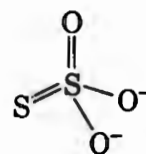
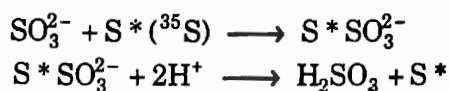


The thiosulphate ion is structurally similar to the sulphate ion; one oxygen atom has been replaced by sulphur atom. Based on Lewis structure oxidation number +6 has been assigned to central sulphur and -2 for the terminal sulphur. Thus, average oxidation state is +2.

In tetrathionate ion  $S_4O_6^{2-}$ , two of the sulphur atoms present in the ion are in oxidation state 0 (zero) and two are in oxidation state +5. Alternately one can say that  $S_4O_6^{2-}$  is the adduct formed by binding of the Lewis base,  $S_2^{2-}$  to  $SO_3$



Isotopic tracer technique has been used to verify the existence of two types of sulphur in  $S_2O_3^{2-}$ . Sulphite ion ( $SO_3^{2-}$ ) is treated with radioactive isotope ( $^{35}S$ ) and the thiosulphate ion ( $S_2O_3^{2-}$ ) is decomposed by acid.  $^{35}S$  is found to be only in precipitated sulphur. This indicates that sulphur ( $^{35}S$ ) is not distributed with other sulphur is  $S_2O_3^{2-}$

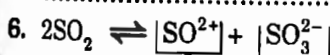


## Target Practice 2

- What are following sulphur allotropes called?  
(a)  $S_\alpha$  ..... (b)  $S_\beta$  .....  
(c)  $S_\gamma$  ..... (d)  $S_\mu$  .....
- $H_2S$  changes to sulphur in Frasch process by reaction  
.....  
....
- Differentiate  $H_2O$  and  $H_2S$  in following properties (smaller/larger)

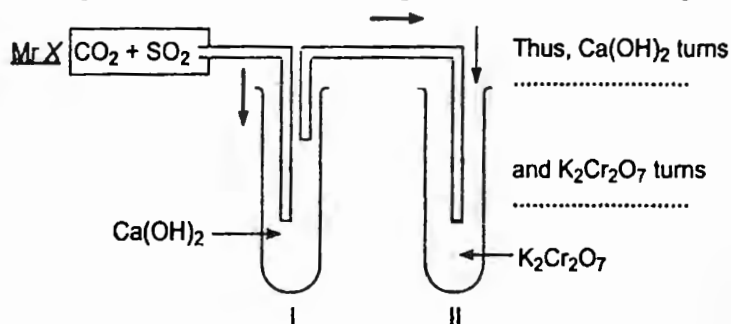
|                   | $H_2O$               | $H_2S$               |
|-------------------|----------------------|----------------------|
| (a) Boiling point | <input type="text"/> | <input type="text"/> |
| (b) Bond angle    | <input type="text"/> | <input type="text"/> |
| (c) Acid-strength | <input type="text"/> | <input type="text"/> |

- $H_2S$  gas is passed into aqueous solution  
(a)  $CuCl_2$  solution (b)  $ZnCl_2$  solution  
 $\downarrow H_2S$   $\downarrow H_2S$   
 $CuS$  is precipitated  $ZnS$  is precipitated  
 Yes/No  Yes/No
- Oxide of sulphur are part of acid rain. Represent phenomenon of acid rain by chemical reaction  
.....  
.....



Name the cation and anion.

- Write the formulae of  
(a) Pyrosulphuric acid .....  
(b) Peroxosulphuric .....  
(c) Peroxodisulphuric acid .....
- Equivalent weight of  $SO_2$  is found to be 32 in a reaction taking place in acidic medium. This reaction is represented as .....
- A gaseous mixture of  $CO_2$  and  $SO_2$  was to be identified in a laboratory. Mr X and Mr Y performed following experiments with common reagents but at different stages.



- Thus,  $K_2CrO_7$  turns .....  
and  $Ca(OH)_2$  turns .....
- Sulphuric acid is produced by lead chamber process with following exothermic reaction



- (a) What is the role of NO?  
.....
- (b) What is the intermediate?  
.....
- (c) Formation of  $\text{H}_2\text{SO}_4$  is favoured under following conditions (higher/lower)  
..... pressure  
..... temperature  
..... concentration of  $\text{SO}_2$ ,  $\text{O}_2$ .

1. (a) Rhombic (b) Monoclinic (c) Liquid (d) Liquid

2.  $2\text{H}_2\text{S}(g) + \text{SO}_2(g) \longrightarrow 3\text{S}(g) + 2\text{H}_2\text{O}(g)$

3. Refer text

4. (a) Yes, because acidic (HCl) medium is formed in which CuS is insoluble.



(b) No, because acidic (HCl) medium is formed in which ZnS is soluble



5.  $\text{SO}_2 + \text{H}_2\text{O} \xrightarrow{\text{rain}} \text{H}_2\text{SO}_3$   
acid rain

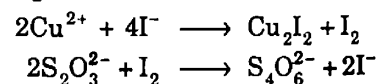
$\text{SO}_3 + \text{H}_2\text{O} \xrightarrow{\text{rain}} \text{H}_2\text{SO}_4$   
acid rain

6.  $\text{SO}_4^{2-}$  : Sulphate  
 $\text{SO}_3^{2-}$  : Sulphite

7. (a)  $\text{H}_2\text{S}_2\text{O}_7$  (b)  $\text{H}_2\text{SO}_5$  (c)  $\text{H}_2\text{S}_2\text{O}_8$

11. Hypo dissolves unreacted AgBr of the photographic film by reaction

12. In the following



(a) equivalent mass of  $\text{Cu}^{2+}$  is .....

(b) equivalent mass of  $\text{S}_2\text{O}_3^{2-}$  is .....

## Answers

8.  $\text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$

9. Mr X : Both  $\text{CO}_2$  and  $\text{SO}_2$  react with  $\text{Ca}(\text{OH})_2$  and lime water turns milky. No effect on  $\text{K}_2\text{Cr}_2\text{O}_7$ .

Mr Y :  $\text{SO}_2$  turns  $\text{K}_2\text{Cr}_2\text{O}_7$  green and  $\text{CO}_2$  does not react at this stage.  $\text{CO}_2$  reacts at stage II with  $\text{Ca}(\text{OH})_2$  and it turns milky.

10. (a) Catalyst

(b)  $\text{NO}_2$

(c) Higher pressure

Lower temperature (theoretically)

Higher concentration of  $\text{SO}_2$  and  $\text{O}_2$

11.  $\text{AgBr} + 2\text{S}_2\text{O}_3^{2-} \longrightarrow [\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-} + \text{Br}^-$

12. (a)  $2\text{Cu}^{2+} \equiv \text{I}_2 \equiv 2\text{I}$

$\therefore \text{Cu}^{2+} \equiv 1$

equivalent mass of  $\text{Cu}^{3+} \equiv \text{ionic weight}$

(b)  $2\text{S}_2\text{O}_3^{2-} \equiv \text{I}_2 \equiv 2\text{I}$

$\therefore \text{S}_2\text{O}_3^{2-} \equiv 1$

$\therefore \text{Equivalent mass of } \text{S}_2\text{O}_3^{2-} = \text{ionic weight.}$

## Practice Exercise 2

1. You have been given an inorganic mixture with a knowledge that group II is absent, but when pass  $\text{H}_2\text{S}$  gas into the mixture solution acidified with dil. HCl, yellowish turbidity appears. Explain.

2.  $\text{FeCl}_3$  solution gives blood red colour with  $\text{NH}_4\text{SCN}$ . If  $\text{H}_2\text{S}$  gas is passed and filtered then filtrate does not give red colour with  $\text{NH}_4\text{SCN}$ . Explain.

3.  $\text{SO}_2$  and  $\text{Cl}_2$  both are used as bleaching agent. What factors cause bleaching?

4. When  $\text{H}_2\text{S}$  gas is passed into  $\text{SO}_2$  in aqueous solution, colloidal yellowish white turbidity appears. Write reaction. Calculate weight of this turbidity if 11.2 L of each gas reacts at NTP.

5.  $4\text{FeS} + 7\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3 + 4\text{SO}_2$   
 $\text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ + 3\text{SO}_2 \longrightarrow 2\text{Cr}^{3+} + 3\text{SO}_4^{2-} + \text{H}_2\text{O}$

1 g sample of FeS was roasted and  $\text{SO}_2$  thus formed required 10 mL of 0.05 M  $\text{K}_2\text{Cr}_2\text{O}_7$  solution in acidic medium. Calculate percentage of FeS in the given sample. (Fe = 56, S = 32)

6. Give examples of reactions for preparing  $\text{SO}_2$  that

(a) are attended by a change in oxidation state of sulphur

(b) are not attended by a change in its oxidation state

7. Sodium salt (A) of a dibasic acid  $\xrightarrow{\text{HCl}}$  gas (B)

Gas (B) turns  $\text{K}_2\text{Cr}_2\text{O}_7$  green and also lime water milky. Identify (A) and (B).

8. How will you estimate  $\text{NaHSO}_3$  volumetrically?

9. What is structure of  $\text{SO}_3^{2-}$  ion?

10.  $\text{Cl}_2$  also behaves as bleaching agent like  $\text{H}_2\text{SO}_3$  (aq  $\text{SO}_2$ ). Explain.

11. How will you identify  $\text{SO}_3^{2-}$  in presence of  $\text{CO}_3^{2-}$ ?

12. Which of nitric acid and sulphuric acid is the stronger Bronsted acid, i.e., which donates proton to the other?

13. Zinc reacts with dil  $\text{H}_2\text{SO}_4$  to give  $\text{H}_2$ . It also reacts with conc  $\text{H}_2\text{SO}_4$  to give  $\text{SO}_2$ . Make difference between these two reactions.





# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** Zinc dissolves in dil HCl to liberate  $H_2(g)$ , but from conc  $H_2SO_4$ ,  $SO_2$  is evolved. Explain.

**Solution** (A)  $Zn + 2H^+ \xrightarrow{\text{dil}} Zn^{2+} + H_2$   $E^\circ = 0.76 \text{ V}$

(B)  $Zn + SO_4^{2-} + 4H^+ \longrightarrow 2H_2O + SO_2 + Zn^{2+}$   
 $E^\circ = 0.93 \text{ V}$

$E^\circ$  of reaction (B) is large than that of (A).

In conc.  $H_2SO_4$ ,  $SO_4^{2-}$  is a better oxidising agent than  $H^+$ . Hence, with conc.  $H_2SO_4$ , reaction (B) predominates.

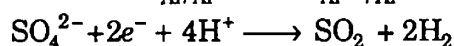
**Problem 2.**  $E^\circ_{Al^{3+}/Al} = -1.66 \text{ V}$ ;  $E^\circ_{SO_4^{2-}/SO_2} = 1.17 \text{ V}$ .

What, if anything, would happen if you reacted aluminium with sulphuric acid? If you think a reaction would take place, write down the equation.

**Solution** The given reaction (say dissolution of Al into  $H_2SO_4$ ) is possible if  $E^\circ_{\text{cell}}$  is positive.

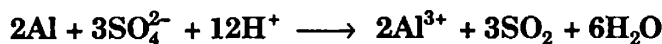


$$E^\circ_{Al/Al^{3+}} = -E^\circ_{Al^{3+}/Al} = 1.66 \text{ V}$$



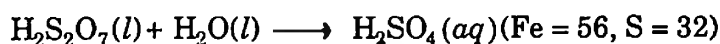
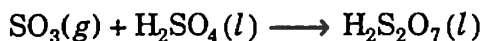
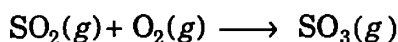
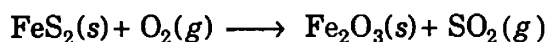
$$E^\circ_{SO_4^{2-}/SO_2} = 1.17 \text{ V}.$$

Net reaction is

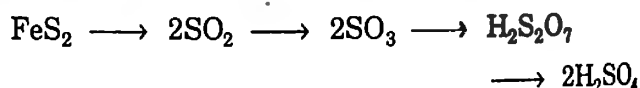


Thus,  $E^\circ_{\text{cell}}$  is 2.83 V hence, Al can reduce  $SO_4^{2-}$  to  $SO_2$ .

**Problem 3.** What mass of  $H_2SO_4$  could be produced in the process given below if 1.00 kg of  $FeS_2$  is used? The unbalanced equations for the process are:



**Solution** Sulphuric acid contains one sulphur atom per molecule, and each  $FeS_2$  molecule gives two atoms of sulphur. Thus,



Thus, 1 mol of  $FeS_2$  gives = 2 mol  $H_2SO_4$   
 $= 2 \times 98 \text{ g } H_2SO_4$

Hence, 1.00 kg  $FeS_2 = 1000 \text{ g } FeS_2 = \frac{1000}{120} \text{ mol } FeS_2$

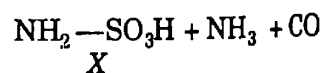
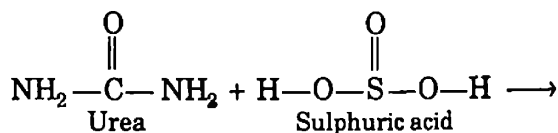
$$H_2SO_4 \text{ from } \frac{1000}{120} \text{ mol } FeS_2 = \frac{2 \times 98 \times 1000}{120} \text{ g}$$

$$= 1.63 \text{ kg } H_2SO_4$$

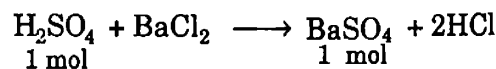
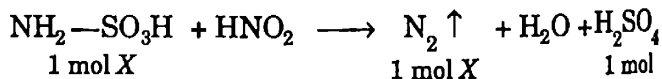
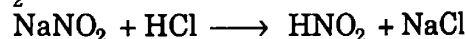
**Problem 4.** The action of concentrated sulphuric acid on urea ( $NH_2CONH_2$ ) results in the production of a white crystalline solid X of formula  $H_3NO_3S$ . This is a monobasic acid. On treatment with sodium nitrate and dilute hydrochloric acid at  $0^\circ \text{C}$  it liberates 1 mol of  $N_2$  per mol of X, and on addition of aqueous barium chloride the resulting solution yields 1 mol of  $BaSO_4$  per mol of X taken.

Deduce the structure of X.

**Solution**  $NH_2CONH_2$  (Urea) reacts with conc.  $H_2SO_4$  forming X ( $H_3NO_3S$ ). X contains one ionisation H (since, X is a monobasic acid). Thus,



X contains free  $-NH_2$  as well as free  $-SO_3H$ . ( $NaNO_2 + HCl$ ) converts free  $-NH_2$  into free  $-OH$  group liberating  $N_2$ .

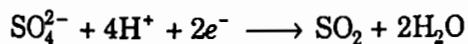
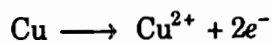


Thus X is  $NH_2 - SO_3H$  (amino sulphonic acid), 1 mol of which liberated 1 mol of  $N_2$  on reaction with ( $NaNO_2 + HCl$ ) at  $0^\circ \text{C}$  and in turn resulting solution gives 1 mol of  $BaSO_4$  on reaction with  $BaCl_2$ .

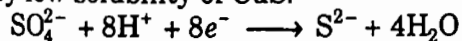
**Explanation**

(a) When metallic copper is heated with conc. sulphuric acid, in addition to copper(II) sulphate,  $\text{CuSO}_4$ , and sulphur dioxide  $\text{SO}_2$ , some copper(II) sulphide,  $\text{CuS}$ , is also formed.

— When conc  $\text{H}_2\text{SO}_4$  is used, Cu is oxidised to  $\text{Cu}^{2+}$  and  $\text{SO}_4^{2-}$  is reduced to  $\text{SO}_2$ .



There is also side reaction assisted by very high  $[\text{H}^+]$  and very low solubility of  $\text{CuS}$ .



(b) The S—OH and S—O distance in the tetrahedral species are as follows:

|                            | S—OH (Å) | S—O (Å) |
|----------------------------|----------|---------|
| $\text{H}_2\text{SO}_4(g)$ | 1.54     | 1.42    |
| $\text{HSO}_4^-$           | 1.56     | 1.47    |
| $\text{SO}_4^{2-}$         | —        | 1.49    |

**Comment on the increase in S—O bond length.**

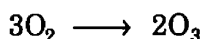
— As the  $\pi$ -bonding is distributed over a larger number of atoms, bond order decreases resulting in an increase in bond length.

# Master Exercises

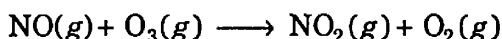
## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

- Give the names and formulae of the compounds in which sulphur exhibits an oxidation state of:-  
(a) -2      (b) +4      (c) +6
- Explain why  $\text{SCl}_6$ ,  $\text{SBr}_6$  and  $\text{SI}_6$  cannot be prepared?
- Give applications of  $\text{O}_3$ .
- What is the change in oxidation number for the following reaction?



- One of the steps involved in the depletion of ozone in the stratosphere by nitric oxide (NO) may be represented as:



What is change in oxidation number of N and O?

- After the ozonisation of a certain volume of oxygen, the volume of the oxygen was found to diminish by 500 mL. What volume of ozone was formed? What amount of heat was absorbed in its formation if  $\Delta H_f^\circ$  is  $144.2 \text{ kJ mol}^{-1}$  for ozone? Assume values at STP.
- Black (A) +  $\text{H}_2\text{SO}_4 \longrightarrow$  gas (B) + (C)  
(B) +  $(\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow$  black ppt (D)  
(C) +  $\text{K}_3[\text{Fe}(\text{CN})_6] \longrightarrow$  blue (E)  
(C) also decolorises acidified  $\text{KMnO}_4$ . Identify (A) to (E).
- What properties does  $\text{H}_2\text{S}$  show when it reacts with aqueous solution of  $\text{KMnO}_4$ ,  $\text{H}_2\text{O}_2$  and  $\text{NaOH}$ ?
- Acid salt (A)  $\xrightarrow{\text{heat}}$  (B)  $\xrightarrow{\text{HCl}}$  Gas (C)  $\xrightarrow{\text{Cr}_2\text{O}_7^{2-}/\text{H}^+}$  Green (G)  
Molar mass       $\downarrow \text{BaCl}_2$        $\downarrow \text{Ca}(\text{OH})_2$   
104      White ppt (D)      Milky  
             soluble in HCl       $\downarrow$  Gas (C)  
              $\downarrow$        $\downarrow$   
             White ppt (H)      Soluble (F)  
Identify (A) to (H) in the above sequence of reactions.

- Which of the following desiccants can be used to remove moisture from  $\text{SO}_2$ : conc.  $\text{H}_2\text{SO}_4$ ;  $\text{KOH}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{K}_2\text{CO}_3$ ?

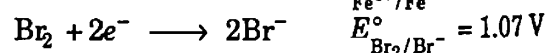
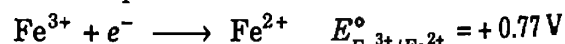
- Conc.  $\text{H}_2\text{SO}_4$  can't be used for drying up  $\text{H}_2\text{S}$  and  $\text{NH}_3$ . Explain.

### Analytical Questions

- $\text{O}_3(g)$  is a powerful oxidising agent. Write equations to represent oxidation of :  
(a)  $\text{I}^-$  to  $\text{I}_2$  in acidic solution.  
(b)  $[\text{Fe}(\text{CN})_6]^{4-}$  to  $[\text{Fe}(\text{CN})_6]^{3-}$  in basic solution.  
(c) S in the presence of moisture to  $\text{H}_2\text{SO}_4$ .
- It has been estimated that if all the  $\text{O}_3$  in the atmosphere were brought to sea level at STP, the gas would form a layer 0.3 cm thick. Estimate the number of  $\text{O}_3$  molecules in the earth's atmosphere. (radius of the earth = 4000 miles; 1 km = 0.6214 mile)
- The redox reaction involving the reducing power of hydrogen sulphide is :



Two other half equations are :



Under standard conditions :

- will hydrogen sulphide react with iron (III) ions?
- will it react with bromine?

If you decide a reaction should take place, write the equation.

- Explain :

- Oxygen is never more than divalent, but S, Se and Te can form four or six bonds.
- $\text{SO}_2$  is gas but  $\text{SeO}_2$  is a solid at room temperature.
- $\text{SF}_6$  is unreactive but  $\text{TeF}_6$  is readily hydrolysed by water.

- (iv) The melting point and boiling point show the sequence :  

$$\text{H}_2\text{O} \gg \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$$
- (v) Acidity increases in the sequence :  

$$\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} \leq \text{H}_2\text{Te}$$
- (vi) The bond angle decreases in the order :  

$$\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se}$$
- (vii) Liquid oxygen sticks to the poles of a magnet but liquid nitrogen does not.  
 [Hint : By MO theory,  $\text{O}_2$  is paramagnetic]
- (viii) The O—O bond in  $\text{O}_2\text{F}_2$  is much shorter than that in  $\text{H}_2\text{O}_2$ .
- (ix) The two sulphur atoms in thiosulphate ion are not identical.
5. Account for the following facts:  
 (a)  $\text{H}_2\text{SO}_4$  is a stronger acid than  $\text{H}_2\text{SO}_3$   
 (b)  $\text{SF}_4$  exists, but  $\text{OF}_4$  does not.  
 (c) The  $\text{S}_8$  ring is non-planar.
6. How many litres of  $\text{SO}_2$  taken in standard conditions have to be passed through a solution of  $\text{HClO}_4$  to reduce 16.9 g of it to  $\text{HCl}$ ?
7. Which of the compounds listed below enter into a reaction with  $\text{Na}_2\text{S}_2\text{O}_3$ ?  
 (a)  $\text{HCl}$  (b)  $\text{NaCl}$   
 (c)  $\text{NaI}$  (d)  $\text{I}_2$   
 (e)  $\text{KMnO}_4$  if:  
 (1) the initial substance becomes decolorised,  
 (2) a precipitate forms,  
 (3) a gas evolved.
8. Oxides and peroxides are not the only types of compounds that metals can make with oxygen, superoxides are also possible. 1.15 g of sodium on reaction with oxygen at high pressure gives 2.75 g of a white powder, sodium superoxide.  
 (i) What mass of oxygen was combined with the sodium?  
 (ii) How many moles of oxygen atoms in this?  
 (iii) How many moles of sodium were used?  
 (iv) What is the formula of the oxide and superoxide ion?

## Exercise 2

### (Stage 2 : High Skill Problem Solving)

#### Only One Option Correct

- Oil of vitriol is  
 (a)  $\text{HNO}_3$  (b)  $\text{HCl}$   
 (c)  $\text{H}_2\text{SO}_4$  (d)  $\text{H}_3\text{PO}_4$
- Which of the following has peroxy linkage?  
 (a)  $\text{H}_2\text{S}_2\text{O}_3$  (b)  $\text{H}_2\text{SO}_5$   
 (c)  $\text{H}_2\text{S}_2\text{O}_7$  (d)  $\text{H}_2\text{S}_4\text{O}_6$
- Which of the following can be used as dehydrating agents?  
 (a) Conc.  $\text{H}_2\text{SO}_4$  (b)  $\text{POCl}_3$   
 (c)  $\text{P}_2\text{O}_5$  (d) All of these
- The thermal stability of hydrides of oxygen family is in order  
 (a)  $\text{H}_2\text{Po} < \text{H}_2\text{Te} < \text{H}_2\text{Se} < \text{H}_2\text{S} < \text{H}_2\text{O}$   
 (b)  $\text{H}_2\text{Po} < \text{H}_2\text{O} < \text{H}_2\text{Te} < \text{H}_2\text{Se} < \text{H}_2\text{S}$   
 (c)  $\text{H}_2\text{S} < \text{H}_2\text{O} < \text{H}_2\text{Te} < \text{H}_2\text{Se} < \text{H}_2\text{Po}$   
 (d)  $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Te} < \text{H}_2\text{Se} < \text{H}_2\text{Po}$
- In case of oxygen family (Group 16)  
 (a) the tendency for catenation decreases markedly as we go down the group  
 (b) maximum coordination of oxygen is four due to lack of  $d$ -orbital but that of other elements is six due to presence of  $d$ -orbital  
 (c) the tendency to form multiple bonds with C, N and O decreases as going down the group from S to Te.  
 (d) all of the above are correct statements
- Which does not have (S—S) bond?  
 (a)  $\text{H}_2\text{S}_2\text{O}_3$  (b)  $\text{H}_2\text{S}_2\text{O}_5$   
 (c)  $\text{H}_2\text{S}_2\text{O}_4$  (d)  $\text{S}_3\text{O}_9$
- Which has maximum  $\text{p}K_a$  value?  
 (a)  $\text{H}_2\text{O}$  (b)  $\text{H}_2\text{S}$   
 (c)  $\text{H}_2\text{Se}$  (d)  $\text{H}_2\text{Te}$
- Consider the following species :  
 1.  $[\text{O}_2]^{2-}$  2.  $[\text{CO}]^+$   
 3.  $[\text{O}_2]^+$   
 Among these species sigma bond alone is present in  
 (a) 1, 2, and 3 (b) 2 alone  
 (c) 2 and 3 (d) 1 alone
- Which of the following species have undistorted octahedral structures?  
 1.  $\text{SF}_6$  2.  $\text{PF}_6^-$   
 3.  $\text{SiF}_6^{2-}$  4.  $\text{SeF}_6$   
 Select the correct answer using the codes given below  
 (a) 2, 3 and 4 (b) 1, 3 and 4  
 (c) 1, 2 and 3 (d) 1, 2 and 4

10. Consider the following compounds

1. Sulphur dioxide
2. Hydrogen peroxide
3. Ozone

Among these compounds, those which can act as bleaching agents would include

- (a) 1 and 3
- (b) 2 and 3
- (c) 1 and 2
- (d) 1, 2 and 3

11. A considerable part of the harmful UV rays of the sun does not reach the surface of the earth. This is because high above the earth's atmosphere, there is a layer of

- (a)  $O_3$
- (b)  $CO_2$
- (c)  $SO_2$
- (d)  $NO$

12. Hypervalent ion is/are

- (a)  $SO_3^{2-}$
- (b)  $PO_4^{3-}$
- (c)  $SO_4^{2-}$
- (d)  $ClO_4^-$

13. Which is/are true statements?

- (a) Sulphur trioxide exists as cyclic trimer in solid state,  $S_3O_9$
- (b) Selenium trioxide solid is a cyclic tetramer,  $Se_4O_{12}$
- (c)  $TeO_3$  is a solid with a network structure in which  $TeO_6$  octahedra share all vertices
- (d) All of the above are correct

14. Which is thermochromic?

- (a)  $S_4N_4$
- (b)  $B_3N_3H_6$
- (c)  $S_8$
- (d) None of these

15. The best reducing agent of the following is

- (a)  $H_2S$
- (b)  $Cl^-$
- (c)  $SO_4^{2-}$
- (d)  $O_3$

16. All of the following have a tetrahedral shape except

- (a)  $SO_4^{2-}$
- (b)  $XeF_4$
- (c)  $ClO_4^-$
- (d)  $XeO_4$

17. The term 'thio' is used in the names of all of the following compounds except

- (a)  $Na_2S_2O_3$
- (b)  $NaCS_3$
- (c)  $NaSCN$
- (d)  $Na_2SO_3$

18. Cold solution of barium nitrite on mixing with sulphuric acid produces

- (a)  $BaSO_4 + HNO_2$
- (b)  $BaSO_4 + HNO_3$
- (c)  $BaSO_4 + NO_2$
- (d)  $BaSO_4 + N_2 + O_2$

19. Which of the following product is formed by the reaction of sulphur dioxide with chlorine in presence of sunlight?

- (a)  $SO_2Cl$
- (b)  $SO_2Cl_2$
- (c)  $SOCl_2$
- (d)  $SO_3Cl$

20. Which of the following bonds has the least energy?

- (a)  $Se-Se$
- (b)  $Te-Te$
- (c)  $S-S$
- (d)  $O-O$

21. Oxalic acid on heating with conc.  $H_2SO_4$  produce

- (a)  $H_2O$  and  $CO_2$
- (b)  $CO$ ,  $CO_2$  and  $H_2O$
- (c)  $CO_2$  and  $H_2S$
- (d)  $CO$  and  $CO_2$

22. Which of the following is not a chalcogen?

- (a)  $Se$
- (b)  $O$
- (c)  $S$
- (d)  $Na$

23. Which of the following gas is insoluble in water?

- (a)  $SO_2$
- (b)  $H_2$
- (c)  $NH_3$
- (d)  $CO_2$

24. Which one of the following acid possesses oxidising, reducing and complex forming properties?

- (a)  $HNO_3$
- (b)  $HCl$
- (c)  $H_2SO_4$
- (d)  $HNO_2$

25.  $Na_2CO_3$  reacts with  $SO_2$  in alkaline medium to produce

- (a)  $Na_2SO_4$
- (b)  $Na_2SO_3$
- (c)  $NaHSO_4$
- (d)  $NaHSO_3$

26. The number of S—S bonds in sulphur trioxide trimer,  $(S_3O_9)$  is

- (a) three
- (b) two
- (c) one
- (d) zero

27. Sulphur dioxide levels in the atmosphere can be reduced by using

- (a) catalytic converters in industry
- (b) static electricity to attract it in factory chimneys
- (c) more efficient car-engines
- (d) low-sulphur fuels

28. What does Green Chemistry in terms of environment mean?

- (a) Greenhouse effect
- (b) Reactions related to depletion of ozone layer
- (c) Photosynthetic reactions in plants
- (d) Reduction in the use and production of hazardous chemicals

29. Which one of the following compounds is not a protonic acid?

- (a)  $SO(OH)_2$
- (b)  $SO_2(OH)_2$
- (c)  $B(OH)_3$
- (d)  $Po(OH)_3$

30. Which of the following gas mixture is used by the divers inside the sea?

- (a)  $O_2 + He$
- (b)  $O_2 + Xe$
- (c)  $O_2 + Ar$
- (d)  $O_2 + N_2$

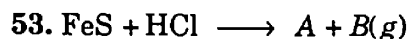
31. A group 16 element exists in the monoatomic state in metallic lattice. It also exists in two crystalline forms. The metal is

- (a) sulphur
- (b) polonium
- (c) selenium
- (d) tellurium

32. To a piece of charcoal sulphuric acid is added. Then

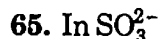
- (a) there is no reaction
- (b) water gas is formed

- (c)  $\text{SO}_2$  and  $\text{CO}_2$  are evolved  
(d)  $\text{CO}$  and  $\text{SO}_2$  are evolved
33. The correct order of O—O bond length in  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  is  
(a)  $\text{H}_2\text{O}_2 > \text{O}_3 > \text{O}_2$  (b)  $\text{O}_2 > \text{H}_2\text{O}_2 > \text{O}_3$   
(c)  $\text{O}_3 > \text{H}_2\text{O}_2 > \text{O}_2$  (d)  $\text{O}_2 > \text{O}_3 > \text{H}_2\text{O}_2$
34. Which of the following is used in vulcanization of rubber?  
(a)  $\text{SF}_6$  (b)  $\text{CF}_4$   
(c)  $\text{Cl}_2\text{F}_2$  (d)  $\text{C}_2\text{F}_2$
35. Aqueous solutions of hydrogen sulphide and sulphur dioxide when mixed together yield  
(a) sulphur trioxide and water  
(b) presence of  $d$ -orbital  
(c) sulphur and water  
(d) hydrogen peroxide and sulphur
36. Which of the following have highest melting points?  
(a)  $p$ -block elements (b)  $s$ -block elements  
(c)  $d$ -block elements (d) None of these
37. Electron affinity is positive, when  
(a) O changes into  $\text{O}^-$   
(b)  $\text{O}^-$  changes into  $\text{O}^{2-}$   
(c) O changes into  $\text{O}^+$   
(d) electron affinity is always negative
38. Consider the following compounds  
1.  $\text{Na}_2\text{S}_2\text{O}_3$   
2.  $\text{Na}_2\text{S}_4\text{O}_6$   
3.  $\text{CaOCl}_2$   
Among these compounds identify those that have different oxidation states for same type of atoms  
(a) 1 and 3 (b) 1 and 3  
(c) 1 and 2 (d) 1, 2 and 3
39. Select correct statement(s).  
(a)  $\text{O}_3$  molecule is resonance stabilised  
(b) There is 3-centre, 4-electron  $\pi$ -bond system in  $\text{O}_3$   
(c) Ozone layer is being depleted by fluorocarbons  
(d) All the above are correct statements
40. Alkali ozonides are  
(a) paramagnetic in nature  
(b) hydrolytically unstable and decompose to superoxides  
(c) decreasing in stability as size of alkali metal decreases  
(d) having all the above statements as correct
41. Among  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , acidity of  $\text{H}_2\text{O}$  is maximum because  
(a) oxygen contains two lone pairs of electrons  
(b) bond angle in  $\text{H}_2\text{O}$  is less than  $109^\circ 28'$  due to VSEPR  
(c) oxygen is more electronegative than C or N  
(d)  $\text{H}_2\text{O}$  is an associated liquid
42. An experiment involving absorption of oxygen and its quantitative estimation would involve use of  
(a) caustic soda (b) pyrogallol  
(c) conc sulphuric acid (d) turpentine oil
43. Maximum coordination number of oxygen in liquid water is  
(a) two (b) three  
(c) four (d) five
44. The colour of the red glass traffic signals is due to  
(a)  $\text{Sb}_2\text{S}_3$  (b)  $\text{HgI}_2$   
(c)  $\text{CdS}$  (d)  $\text{CdSe}$
45. There is  $p\pi-d\pi$  multiple bonding in  
(a)  $\text{CS}_2$  (b)  $\text{CO}_2$   
(c)  $\text{NO}_2$  (d)  $\text{NO}$
46. Ozone reacts with all the following reagents except one of the following  
(a)  $\text{K}_2\text{MnO}_4$   
(b) moist iodine  
(c) potassium ferrocyanide  
(d) mercury
47. The absorption of UV radiation by  $\text{O}_3$   
(a) protects the inhabitants of our planet from injurious radiation  
(b) maintains an equilibrium between the concentrations of  $\text{O}_2$  and  $\text{O}_3$   
(c) makes both the function effective  
(d) makes no function effective
48. Ozone layer is being depleted. This is due to  
(a) No emission from supersonic jets  
(b) chlorofluorocarbon used as aerosols  
(c) both (a) and (b)  
(d) None of the above
49. Estimation of ozone can be made quantitatively by  
(a) decomposition into  $\text{O}_2$  and absorption of  $\text{O}_2$  into pyrogallol  
(b) volumetric method using KI and titration of the liberated iodine using hypo solution  
(c) oxidative ozonolysis method  
(d) all methods given above
50. Oxidative ozonolysis of 2-butene in presence of Zn or dimethyl sulphide forms  
(a)  $\text{CH}_3\text{CHO}$  (b)  $\text{CH}_3\text{COOH}$   
(c)  $\text{CO}_2$  (d)  $(\text{CH}_3)_2\text{CO}$
51. The process of obtaining sulphur by the borehole method is called  
(a) the Frasch process  
(b) the Lablanc process  
(c) the Calcaroni process  
(d) the Mannheim process
52. When molten sulphur is suddenly cooled by pouring into water, it takes the form of  
(a) milk of sulphur (b) colloidal sulphur  
(c) flower of sulphur (d) plastic sulphur



Gas B is passed into aqueous solution of C to form A  
Select correct statements based on the above facts

- Colour of C changes from yellow to very light green
  - Gas B turns lead acetate paper black
  - A form deep blue colour with  $\text{K}_3[\text{Fe}(\text{CN})_6]$
  - All the above facts are true
54. Yellow oils of sulphur is/are
- $\text{H}_2\text{S}$
  - $\text{H}_2\text{S}_2, \text{H}_2\text{S}_3$
  - $\text{H}_2\text{SO}_4$
  - $\text{CS}_2, \text{NH}_2\text{CSNH}_2$
55.  $\text{H}_2\text{S}$  precipitates aqueous  $\text{ZnCl}_2$  solution in
- acidic medium
  - neutral medium
  - both (a) and (b)
  - None of these
56. In presence of  $\text{H}_2\text{O}$ ,  $\text{SO}_2$  acts as
- an oxidising agent
  - a reducing agent
  - a hydrolysing agent
  - a redox reagent
57.  $\text{SO}_2$  behaves as a reducing agent when
- passed over hot  $\text{CuO}$
  - mixed with moist  $\text{H}_2\text{S}$
  - passed through acidified  $\text{KMnO}_4$  solution
  - passed through  $\text{FeSO}_4$  solution
58. When an article is bleached by  $\text{SO}_2$  it loses its colour. The colour can be restored by
- exposure to air
  - heating
  - dilution
  - None of these
59. The compound of sulphur used as a solvent in rubber industry is
- $\text{SO}_2(\text{OH})\text{Cl}$
  - $\text{SO}_2$
  - $\text{SO}_3$
  - $\text{S}_2\text{Cl}_2$
60. S—S bond is present in
- $\alpha\text{-(SO}_3)_n$
  - $\gamma\text{-(S}_3\text{O}_9)$
  - $\text{H}_2\text{S}_2\text{O}_3$
  - $\text{H}_2\text{S}_2\text{O}_8$
61. The compound which has no reaction with  $\text{KMnO}_4$  is
- perdisulphuric acid
  - sulphurous acid
  - hydrogen sulphide
  - hydrogen peroxide
62. A bottle completely filled with conc.  $\text{H}_2\text{SO}_4$  is left unstoppered for several days and we observe spontaneous overflow of acid. It is due to
- change in temperature
  - hygroscopic nature of  $\text{H}_2\text{SO}_4$
  - absorption of air by  $\text{H}_2\text{SO}_4$
  - dehydration of  $\text{H}_2\text{SO}_4$
63. Out of  $\text{H}_2\text{S}_2\text{O}_3$ ,  $\text{H}_2\text{S}_4\text{O}_6$ ,  $\text{H}_2\text{SO}_5$  and  $\text{H}_2\text{S}_2\text{O}_8$  peroxy acids are
- $\text{H}_2\text{S}_2\text{O}_3, \text{H}_2\text{S}_4\text{O}_6$
  - $\text{H}_2\text{S}_4\text{O}_6, \text{H}_2\text{SO}_5$
  - $\text{H}_2\text{SO}_5, \text{H}_2\text{S}_2\text{O}_8$
  - $\text{H}_2\text{S}_2\text{O}_3$  and  $\text{H}_2\text{S}_2\text{O}_8$
64. Which of the following can convert acidified  $\text{Cr}_2\text{O}_7^{2-}$  to green?
- $\text{SO}_2/\text{H}_2\text{SO}_3/\text{H}_2\text{SO}_4$
  - $\text{SO}_3/\text{H}_2\text{SO}_3/\text{H}_2\text{S}$
  - $\text{SO}_3^{2-}/\text{H}_2\text{S}/\text{Fe}^{2+}$
  - $\text{S}_2\text{O}_3^{2-}/\text{SO}_3/\text{Fe}^{3+}$



- $d\pi\text{-}p\pi$  bond between S and O is delocalised
  - bonds between S and O are equivalents
  - there is  $sp^3$  hybridised sulphur atom
  - all of the facts given above are true
66. Liver of sulphur is a mixture of
- potassium pentasulphide (A) and potassium thiosulphate (B)
  - potassium carbonate (C) and (B) above
  - potassium disulphide (D) and (B) above
  - (B) and (D) above
67. Bleaching of a fabric cloth is done using A and excess of chlorine is removed using B is
- $\text{CaOCl}_2, \text{Na}_2\text{SO}_3$
  - $\text{Na}_2\text{S}_2\text{O}_3, \text{CaOCl}_2$
  - $\text{CaCl}_2, \text{Na}_2\text{S}_2\text{O}_3$
  - $\text{CaOCl}_2, \text{Na}_2\text{S}_2\text{O}_3$
68.  $\text{Na}_2\text{S}_2\text{O}_3$  is used in photography for fixing the negative. It removes the  $\text{AgBr}$  by
- complex formation  $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$
  - oxidation of  $\text{AgBr}$  to  $\text{Br}_2$
  - reduction of  $\text{AgBr}$  to  $\text{Ag}$
  - formation of double salt
69. Aqueous hyposolution on reaction with aqueous  $\text{AgNO}_3$  gives
- yellow ppt changing to black
  - white ppt changing to black
  - orange ppt changing to blue
  - no ppt
70.  $\text{S}_2\text{O}_3^{2-}$  has
- S—S linkage
  - S—O linkage
  - both (a) and (b)
  - None of these

## Brain Twisters

- Is the same amount of sulphuric acid needed to dissolve 40 g of nickel if we take concentrated acid in one case and dilute acid in another? How many grams of sulphuric acid will go to oxidise the nickel in each case? ( $\text{Ni} = 59$ )
- What mass of  $\text{H}_2\text{SO}_4$  could be produced in the process given below if 1.00 kg of  $\text{FeS}_2$  is used? The unbalanced equations for the process are:
 
$$\text{FeS}_2 + \text{O}_2 \longrightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2$$

$$\text{SO}_2 + \text{O}_2 \longrightarrow \text{SO}_3$$

$$\text{SO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{S}_2\text{O}_7$$

$$\text{H}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$$
- What is equivalent weight of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ?
- Calculate number of moles of  $\text{Na}_2\text{S}_2\text{O}_3$  that will react with  $\text{I}_2$  obtained when 1 mole of  $\text{K}_2\text{Cr}_2\text{O}_7$  reacts with excess of  $\text{KI}$  in acidic medium.

5. Colourless salt (A) decolorises  $I_2$  solution and gives white ppt (changing to black) with  $AgNO_3$  solution. (A) also changes  $FeCl_3$  (yellow) solution to  $FeCl_2$  (green). Identify (A) and explain reactions.
6. A 1.1 g sample of copper ore is dissolved and  $Cu^{2+}(aq)$  is titrated with excess KI. The liberated  $I_2$  requires 12.12 mL of 0.1 M  $Na_2S_2O_3$  for its titration. What is the % copper by mass in the ore?

## Passage Comprehension Questions

### Passage 1

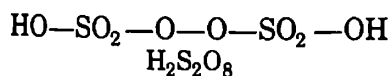
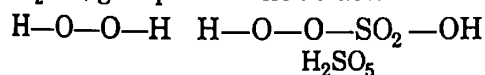
Peroxydisulphuric acid and its salts are powerful oxidising agents, thus can be used to estimate reducing agents and also to study the kinetics of the reaction.

Answer the following questions.

- Peroxydisulphuric acid
  - is also called Marshall's acid
  - has two peroxy linkages
  - liberates  $I_2$  with KI in a fast reaction
  - has oxidation number of sulphur as +7
- As compared to  $H_2SO_5$ ,  $H_2S_2O_8$ 
  - has two peroxy linkage
  - liberates  $I_2$  from KI slowly and thus kinetics of oxidation of KI by  $S_2O_8^{2-}$  can be studied
  - has different oxidation number
  - reacts with  $KMnO_4$

### Passage 2

Two acids have been derived from  $H_2O_2$  by replacing H by  $(SO_3OH)$  group. Both the acids have one peroxy linkage



Based on the above study, answer the following questions.

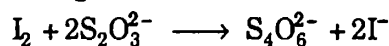
- Which is called Marshall's acid and which is called Caro's acid?
  - $H_2SO_5$ ,  $H_2S_2O_8$
  - $H_2S_2O_8$ ,  $H_2SO_5$
  - $H_2SO_5$ ,  $H_2S_2O_7$
  - $H_2S_2O_3$ ,  $H_2SO_5$
- $H_2S_2O_8$  is obtained at anode by the electrolysis of .....
  - $H_2SO_3$
  - $H_2S_2O_4$
  - $H_2SO_4$
  - $H_2O_2$  and  $H_2SO_4$
- Which reacts with  $KMnO_4$ ?
  - $H_2SO_3$
  - $H_2SO_5$
  - $H_2SO_4$
  - $H_2S_2O_8$

### Passage 3

Sodium thiosulphate is the laboratory reagent used in iodometric and iodimetric titration. This also finds used in photography.

Based on the above passage, answer the following questions.

- In the following reaction



equivalent mass of  $S_2O_3^{2-}$  is (molar mass =  $M$ )

- $M$
  - $\frac{M}{2}$
  - $\frac{M}{3}$
  - $\frac{M}{4}$
- If  $I_2$  is the titre in a titration A and  $I_2$  is formed *in situ* in a titration B, then these are respectively
    - iodometric, iodimetric
    - iodimetric, iodometric
    - both iodimetric
    - both iodometric
  - Sodium thiosulphate is called .....<sup>I</sup> and is used as .....<sup>II</sup> and removes unreacted light sensitive AgBr by forming the complex .....<sup>III</sup>

| I                                | II        | III                   |
|----------------------------------|-----------|-----------------------|
| (a) hypo                         | developer | $[AgS_2O_3]^-$        |
| (b) hypo                         | fixer     | $[Ag(S_2O_3)_2]^{3-}$ |
| (c) hypo                         | fixer     | $[Ag_2(S_2O_3)]$      |
| (d) none of the above is correct |           |                       |

### Passage 4

When metallic copper is heated with conc. sulphuric acid, various types of products are formed depending on standard reduction potential.

Answer following questions based on above study.

- Which reaction is possible?
  - $Cu + 2H^+ \longrightarrow Cu^{2+} + H_2$
  - $Cu^{2+} + H_2 \longrightarrow Cu + 2H^+$
  - Both (a) & (b)
  - None of the above
- When Cu reacts with conc.  $H_2SO_4$ 
  - Cu is oxidised to  $Cu^{2+}$
  - $SO_4^{2-}$  is reduced to  $SO_2$
  - both of the above reactions take place
  - none of the above reaction take place
- There is also formation of CuS which is formed by
  - $SO_4^{2-} + 8H^+ + 8e^- \longrightarrow S^{2-} + H_2O$
  - $SO_2 + 6H^+ + 6e^- \longrightarrow H_2S + 2H_2O$
  - both (a) & (b)
  - None of the above



## Assertion & Reason

**Codes :**

- (a) Both **A** and **R** are true and **R** is the correct explanation of **A**.
  - (b) Both **A** and **R** are true but **R** is not the correct explanation of **A**.
  - (c) **A** is true but **R** is false.
  - (d) **A** is false but **R** is true.
  - (e) **A** and **R** both are false.
1. **Assertion (A) :** Oxygen is the most abundant element on the surface of earth.  
**Reason (R) :** Oxygen is paramagnetic with double bond character.
  2. **Assertion (A) :** Of all the elements of the Group-16, sulphur has the largest tendency to catenation.  
**Reason (R) :** Sulphur-sulphur bond energy is very high.
  3. **Assertion (A) :**  $\text{S}_3\text{O}_6^{2-}$  (trithionate) has S—S bond.  
**Reason (R) :** It is a conjugate base of  $\text{HS}_3\text{O}_6^-$ .
  4. **Assertion (A) :**  $\text{O}_2$  gas is effected in magnetic field.  
**Reason (R) :** It has north and south pole.
  5. **Assertion (A) :**  $\text{SO}_3$  is a nucleophile.  
**Reason (R) :**  $\text{SO}_3$  has lone-pair of electrons.
  6. **Assertion (A) :**  $\text{SO}_2$  turns acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  green.  
**Reason (R) :**  $\text{K}_2\text{Cr}_2\text{O}_7$  is reduced to  $\text{Cr}^{3+}$  (green)salt by  $\text{SO}_2$ .
  7. **Assertion (A) :**  $\text{SO}_2$  is a bleaching agent.  
**Reason (R) :** Nascent oxygen causes bleaching.
  8. **Assertion (A) :** One mole of  $\text{SO}_2\text{Cl}_2$  in aqueous solution is neutralised by 3 moles of  $\text{NaOH}$ .  
**Reason (R) :** 3 moles of  $\text{H}^+$  are formed due to reaction with water.
  9. **Assertion (A) :** Anhydrous sulphuric acid has very high viscosity.  
**Reason (R) :** H-bonding makes it viscous.
  10. **Assertion (A) :** Anhydrous  $\text{H}_2\text{SO}_4$  undergoes autoprotolysis  
$$\text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_3\text{SO}_4^+ + \text{HSO}_4^-$$
  
**Reason (R) :** Anhydrous  $\text{H}_2\text{SO}_4$  has very high electrical conductivity.
  11. **Assertion (A) :** In aqueous solution,  $\text{SO}_2$  reacts with  $\text{H}_2\text{S}$  forming sulphur.  
**Reason (R) :**  $\text{SO}_2$  is an effective reducing agent.

12. **Assertion (A) :** Structure of  $\text{SO}_4^{2-}$  is identical to  $\text{S}_2\text{O}_3^{2-}$ .

**Reason (R) :** Sulphur atoms in  $\text{S}_2\text{O}_3^{2-}$  are in different oxidation states.

## True & False

1. Sulphur is an insulator while selenium and tellurium are semiconductor.
2. Maximum catenation among non-metals is in sulphur.
3.  $\text{O}_2$ ,  $\text{O}_2^-$  are paramagnetic while  $\text{O}_3$ ,  $\text{O}_2^{2-}$  are diamagnetic.
4. There is one (S—S) bond in  $\text{H}_2\text{S}_2\text{O}_8$ .
5.  $\text{S}_4\text{N}_4$  is thermochromic.
6.  $\text{S}_4\text{N}_4$  is kinetically stable but endothermic compound.
7. Peroxy linkage is present in oleum  $\text{H}_2\text{S}_2\text{O}_7$ .
8. Caro's is an oxidising agent.
9.  $\text{SO}_3$  is an electrophile in the sulphonation of benzene.
10. Highest fluorides of oxygen is  $\text{OF}_2$  whereas sulphur forms  $\text{SF}_6$ .
11.  $\text{KO}_2$  is paramagnetic.
12. Bond order of  $\text{O}_2^-$  is 1.5.
13.  $\text{KO}_2$ ,  $\text{BaO}_2$ ,  $\text{Na}_2\text{O}_2$  are superoxides.
14.  $\text{SO}_2$  and  $\text{CO}_2$  both turns lime water milky.
15. Oxygen is by far the most abundant metal on the earth's crust.

## Fill in the Blanks

1. Paramagnetic behaviour is observed in ..... of  $\text{O}_3$ ,  $\text{O}_2$ ,  $\text{NO}$  and  $\text{NO}_2$ .
2. Highly electrical conducting behaviour is present in anhydrous  $\text{H}_2\text{SO}_4$  due to .....
3. Anhydrous  $\text{H}_2\text{SO}_4$  has high viscosity due to .....
4. Peroxy linkage is present in acid .....
5. When Marshall's acid is hydrolysed there is formation of ..... and .....
6. (S—S) bond is present in the acid .....
7. Tetrasulphur tetranitride is .....
8. In group 16 maximum catenation is in .....
9. Common oxidation states of group 16 elements are .....
10. Unlike sulphur which is an ..... selenium and tellurium are .....

11. Superoxide ion is ..... and is ..... in character.
12. Bond orders of  $O_2$ ,  $O_2^-$ ,  $O_2^{2-}$ ,  $O_2^+$  and  $O_2^{2+}$  in increasing order are .....

## Matrix-Match Type Questions

### I. One or More Correct

1. Match the species in Column I with their corresponding properties in Column II.

| Column I |        | Column II |                       |
|----------|--------|-----------|-----------------------|
| A.       | $SO_2$ | 1.        | Oxidant               |
| B.       | $SO_3$ | 2.        | Reductant             |
| C.       | $O_3$  | 3.        | Resonance stabilised  |
| D.       | $H_2S$ | 4.        | $sp^2$ hybridisation  |
| E.       | $H_2O$ | 5.        | $sp^3$ hybridisation  |
|          |        | 6.        | Maximum boiling point |
|          |        | 7.        | Minimum boiling point |

2. Match the acids in Column I with their corresponding properties in Column II.

| Column I |             | Column II |                                |
|----------|-------------|-----------|--------------------------------|
| A.       | $H_2SO_5$   | 1.        | Hydrolysed to give $H_2O_2$    |
| B.       | $H_2SO_4$   | 2.        | Hydrolysed to give $H_2SO_4$   |
| C.       | $H_2S_2O_7$ | 3.        | S—S bond present               |
| D.       | $H_2S_2O_3$ | 4.        | Peroxy linkage present         |
| E.       | $H_2S_2O_8$ | 5.        | S in different oxidation state |
|          |             | 6.        | O in different oxidation state |
|          |             | 7.        | Hygroscopic                    |

## Integer Answer Types

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the ORS have to be darkened. For example, if the correct answers to question number X, Y, Z and W (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will be like the following

| X | Y | Z | W |
|---|---|---|---|
| ① | ① | ① | ① |
| ② | ② | ② | ② |
| ③ | ③ | ③ | ③ |
| ④ | ④ | ④ | ④ |
| ⑤ | ⑤ | ⑤ | ⑤ |
| ⑥ | ⑥ | ⑥ | ⑥ |
| ⑦ | ⑦ | ⑦ | ⑦ |
| ⑧ | ⑧ | ⑧ | ⑧ |
| ⑨ | ⑨ | ⑨ | ⑨ |

### Set I

- $O_2$  is paramagnetic due to ..... unpaired electrons.
- $SO_2$  reduces  $Cr_2O_7^{2-}$  to  $Cr^{3+}$ ; change in oxidation number of Cr is .....
- Maximum oxidation state shown by sulphur in its compounds is .....
- There are equal number of sulphur atoms in thiosulphuric acid, Marshall's acid and oleum. This number is .....
- $SO_2$  reduces  $MnO_4^-$  to  $Mn^{2+}$ . Number of electrons involved in the reduction of  $MnO_4^-$  to  $Mn^{2+}$  is .....
- $SO_2$  turns lime water milky, 3.2 g of  $SO_2$  gives milkiness ..... g.
- One mole of  $SO_2Cl_2$  on hydrolysis gives acids which can be neutralised by ..... moles of NaOH.
- Ozonolysis of 2,5-dimethyl-2,4-hex-diene gives total number of carbonyl compounds .....

### Set II

- 4.35 g of pyrolusite ( $MnO_2$  mineral) is digested with conc. HCl and KI added. Mixture required 5 mL of 1 M  $Na_2S_2O_3$  solution for complete reaction of  $KI_3$  formed. What is % of pure  $MnO_2$  in pyrolusite? (Mn = 55)
- How many S—S bonds are there in  $S_3O_9$ ?
- There are two types of sulphur with different oxidation states in thiosulphate ion. Difference in oxidation states is .....
- Acid rain is due to dissolved non-metallic oxides ( $SO_2$ ,  $NO_2$ ,  $P_2O_5$ , etc). 10 mL of acid rain sample required 5 mL of 0.01 M  $Ca(OH)_2$  for making it neutral. What is pH of acid rain?
- How many  $\widehat{SOS}$  angles are there in  $S_3O_9$ ?
- How many of the following have peroxy linkages?  
 $H_2S_2O_3$ ,  $H_2S_2O_8$ ,  $H_2SO_5$ ,  $CrO_5$ ,  $BaO_2$ ,  $KO_2$
- There is also formation of insoluble CuS (black) when copper reacts with conc.  $H_2SO_4$ . What is change in oxidation number of sulphur?
- How many of the following can be the oxidising agent?  
 $H_2S$ ,  $H_2SO_4$ ,  $H_2SO_3$ ,  $H_2S_2O_3$

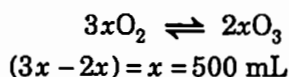
# Answers & Solutions

## Master Exercises

### Exercise 1

#### Short Answer Type Questions

- (a)  $\text{H}_2\text{S}$  (b)  $\text{SO}_2, \text{H}_2\text{SO}_3$   
(c)  $\text{H}_2\text{SO}_4, \text{H}_2\text{SO}_5, \text{H}_2\text{S}_2\text{O}_8, \text{SO}_3$
- Cl, Br and I atoms are too bulky around the sulphur atom.
- It absorbs UV light. It is also used as a disinfectant to purify drinking water, since it destroys bacteria and viruses. *Its advantage over  $\text{Cl}_2$  for this purpose is that it avoids the unpleasant smell and taste of chlorine since any excess  $\text{O}_3$  soon decompose to  $\text{O}_2$ .*
- No change
- $$\begin{array}{ccccccc} \text{N} & \text{O} & + & \text{O}_3 & \longrightarrow & \text{N} & \text{O}_2 + \text{O}_2 \\ \uparrow & \uparrow & & \uparrow & & \uparrow & \uparrow \\ +2 & -2 & & 0 & & +4 & -2 \end{array}$$
- 1000 mL  $\text{O}_3$ , 6.44 kJ

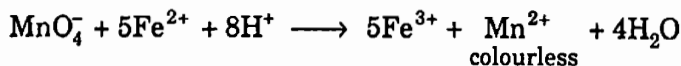


$$\text{Volume of formed } \text{O}_3 = 1000 \text{ mL} = \frac{1000}{22400} \text{ mol}$$

$$= 0.0446 \text{ mol}$$

$$\text{Heat absorbed} = 144.2 \times 0.0446 \text{ kJ} = 6.44 \text{ kJ}$$

- (A) :  $\text{FeS}$  (B) :  $\text{H}_2\text{S}$  (C) :  $\text{FeSO}_4$  (D) :  $\text{PbS}$   
(E) :  $\text{K Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$  **Turnbull's blue**

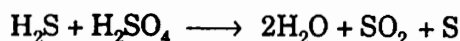


- $\text{MnO}_4^- + \text{H}^+ + \text{H}_2\text{S} \longrightarrow \text{S} + \text{Mn}^{2+}$ ,  $\text{H}_2\text{S}$  is a reducing agent  
 $\text{H}_2\text{S} + \text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{S}$  is a reducing agent  
 $\text{H}_2\text{S} + \text{NaOH} \longrightarrow \text{NaHS} \longrightarrow \text{Na}_2\text{S}$ ,  $\text{H}_2\text{S}$  is a diprotic acid.

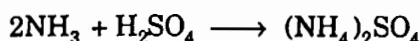
- (A) :  $\text{NaHSO}_3$  (B) :  $\text{Na}_2\text{SO}_3$  (C) :  $\text{SO}_2$  (D) :  $\text{BaSO}_3$   
(E) :  $\text{CaSO}_3$  (F) :  $\text{Ca}(\text{HSO}_3)_2$  (G) :  $\text{Cr}^{3+}$  (H) :  $\text{BaSO}_4$

- $\text{P}_2\text{O}_5$

- $\text{H}_2\text{S}$  is oxidised to S by  $\text{H}_2\text{SO}_4$  (which is reduced to  $\text{SO}_2$ )



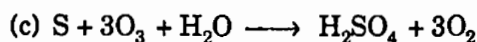
while  $\text{NH}_3$  forms salt with  $\text{H}_2\text{SO}_4$



hence,  $\text{H}_2\text{SO}_4$  can't be used for drying up these gases.

#### Analytical Questions

- (a)  $\text{O}_3 + 2\text{I}^- + 2\text{H}^+ \longrightarrow \text{O}_2 + \text{I}_2 + \text{H}_2\text{O}$   
(b)  $2[\text{Fe}(\text{CN})_6]^{4-} + \text{O}_3 + \text{H}_2\text{O} \longrightarrow 2[\text{Fe}(\text{CN})_6]^{3-} + 2\text{OH}^- + \text{O}_2$



- radius = 4000 miles

$$4000 \text{ miles} = \frac{4000}{0.6214} \text{ km} = \frac{4 \times 10^6}{0.6214} \text{ m}$$

$$\text{thickness} = 0.3 \text{ cm} = 0.003 \text{ m}$$

$$\text{Volume of } \text{O}_3 \text{ molecules at the surface} = 4\pi r^2 \text{ thickness}$$

$$= 4 \times \frac{22}{7} \times \left( \frac{4 \times 10^6}{0.6214} \right)^2 \times 0.003 \text{ m}^3$$

$$V = 1.56273 \times 10^{12} \text{ m}^3$$

$$P = 1 \text{ atm} = 1.01325 \times 10^5 \text{ Pascal}$$

$$\text{Moles} = n = \frac{pV}{RT}$$

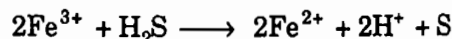
$$= \frac{1.01325 \times 10^5 \times 1.56273 \times 10^{12}}{8.3143 \times 273}$$

$$= 6.976 \times 10^{13}$$

$$\therefore \text{Molecules} = nN_0 = 6.976 \times 10^{13} \times 6.02 \times 10^{23}$$

$$= 4.2 \times 10^{37}$$

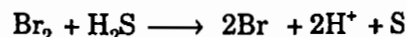
- (i) Yes,  $\text{Fe}^{3+}$  ions will oxidise  $\text{H}_2\text{S}$  to S



$$\text{Since, } E^\circ = 0.77 - 0.14 = 0.63 \text{ V}$$

$$\text{and thus } \Delta G^\circ = -nFE^\circ_{\text{cell}} = -ve$$

- (ii) Yes,  $\text{Br}_2$  also oxidises  $\text{H}_2\text{S}$  to S



$$\text{Since, } E^\circ = 1.07 - 0.14 = 0.93 \text{ V}$$

$$\text{and } \Delta G^\circ = -ve$$

**Note :** A cell reaction is spontaneous

if  $E^\circ_{\text{cell}} = +ve$  and  $\Delta G^\circ = -ve$

$$E^\circ_{\text{cell}} = E^\circ_{\text{ox}} + E^\circ_{\text{red}}$$

(Take values as per half-reactions)

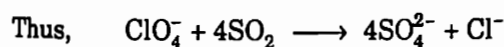
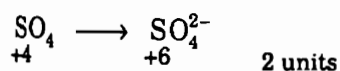
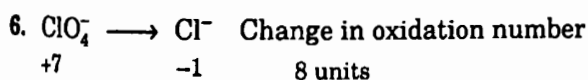
- Refer Text.

- (a) Acid strength increases as the number of O-atoms increases.  
(b) In comparison with S, O is much too electronegative to form compounds of O in +4 oxidation state. Also uses  $sp^3d^2$ -hybrid orbitals for bonding in  $\text{SF}_6$  but O

does not have valence  $d$ -orbitals and it cannot form four bonds to F.

- (c) Each S is  $sp^3$ -hybridised with two lone pair of electrons. The bond angles are  $109.5^\circ$ . A planar ring would require bond angles of

$$= \left(180 - \frac{360}{8}\right) = 135^\circ$$



Since, 1 mol  $\text{HClO}_4$  is reduced by = 4 mol  $\text{SO}_2$

hence,  $16.9 \text{ g} \left( = \frac{16.9}{100.5} \text{ mole} \right) \text{HClO}_4$  is reduced by

$$= \frac{4 \times 16.9}{100.5} \text{ mol SO}_2$$

$$= 0.673 \text{ mol}$$

$$1 \text{ mol of STP} = 22.4 \text{ L SO}_2$$

Thus,  $0.673 \text{ mol at STP} = 22.4 \times 0.673$

$$= 15.067 \text{ L}$$

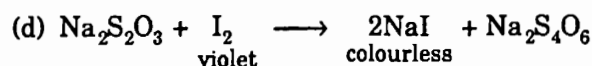


If  $\text{Na}_2\text{S}_2\text{O}_3$  reacts with  $\text{HCl}$ , there is formation of precipitate (S) — thus (2) and formation of gas ( $\text{SO}_2$ ) — thus (3)

(a) — 2, 3

(b) None

(c) None

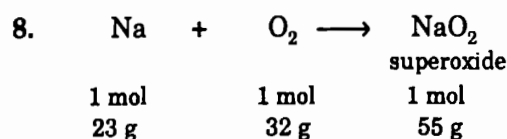


Thus, initial substance is decolourised (1)

Thus, (d) — 1

(e)  $\text{KMnO}_4$  (pink-violet) is also decolourised.

Thus, (e) — 1



$$1.15 \text{ g} = 0.05 \text{ mol} \quad 0.05 \text{ mol}$$

$$2.75 \text{ g} = \frac{2.75}{55} = 0.05 \text{ mol}$$

(i)  $\text{O}_2$  combined =  $0.05 \text{ mol} = 1.6 \text{ g}$

(ii)  $\text{O}_2 = 0.05 \text{ mol} = 0.10 \text{ mol O-atoms}$

(iii) sodium used =  $0.05 \text{ mol}$

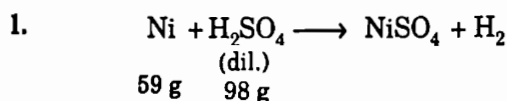
(iv) superoxide =  $\text{NaO}_2$

## Exercise 2

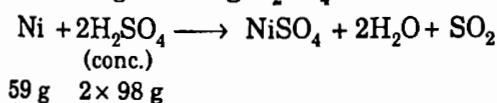
### Only One Option Correct

- |         |         |         |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c)  | 2. (b)  | 3. (d)  | 4. (a)  | 5. (d)  | 6. (d)  | 7. (a)  | 8. (d)  | 9. (d)  | 10. (c) |
| 11. (a) | 12. (d) | 13. (d) | 14. (a) | 15. (a) | 16. (b) | 17. (d) | 18. (a) | 19. (b) | 20. (b) |
| 21. (b) | 22. (d) | 23. (b) | 24. (d) | 25. (b) | 26. (d) | 27. (d) | 28. (d) | 29. (c) | 30. (a) |
| 31. (b) | 32. (c) | 33. (a) | 34. (a) | 35. (c) | 36. (a) | 37. (b) | 38. (d) | 39. (d) | 40. (d) |
| 41. (c) | 42. (b) | 43. (c) | 44. (d) | 45. (a) | 46. (b) | 47. (c) | 48. (c) | 49. (b) | 50. (a) |
| 51. (a) | 52. (d) | 53. (d) | 54. (b) | 55. (b) | 56. (b) | 57. (c) | 58. (a) | 59. (d) | 60. (c) |
| 61. (a) | 62. (b) | 63. (c) | 64. (c) | 65. (d) | 66. (d) | 67. (d) | 68. (a) | 69. (b) | 70. (c) |

### Brain Twisters

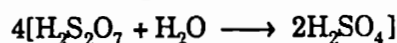
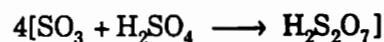
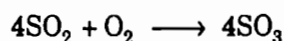
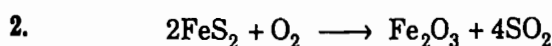


$$40 \text{ g} = 66.44 \text{ g H}_2\text{SO}_4$$



$$40 \text{ g} = 132.88 \text{ g H}_2\text{SO}_4$$

Thus, amount of dil.  $\text{H}_2\text{SO}_4$  and conc.  $\text{H}_2\text{SO}_4$  to dissolve 40 g Ni is different.



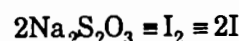
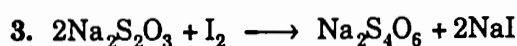
$$2[56 + 64] \text{ g} \equiv 4 \times 98 \text{ g}$$

$$\text{FeS}_2$$

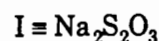
$$1000 \text{ g FeS}_2 \text{ give } = \frac{4 \times 98}{240} \times 1000 \text{ g H}_2\text{SO}_4$$

$$= 1633.33 \text{ g}$$

$$= 1.6333 \text{ kg}$$



Thus,



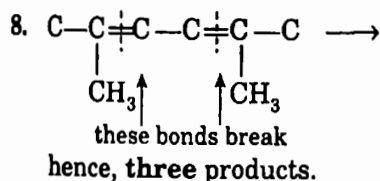
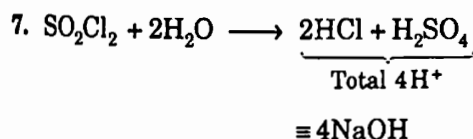
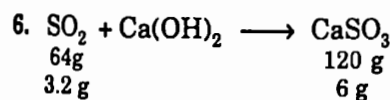
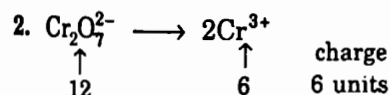


## Integer Answer Types

## Set I

|             |   |   |   |   |   |   |   |   |
|-------------|---|---|---|---|---|---|---|---|
| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Answers →   | 2 | 6 | 6 | 2 | 5 | 6 | 4 | 3 |
|             | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
|             | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|             | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
|             | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
|             | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
|             | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
|             | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
|             | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
|             | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
|             | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |

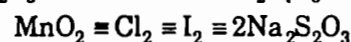
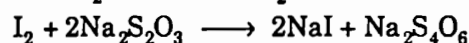
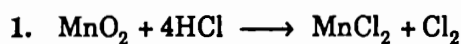
## Hints



## Set II

|             |   |   |   |   |   |   |   |   |
|-------------|---|---|---|---|---|---|---|---|
| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Answers →   | 5 | 0 | 8 | 2 | 3 | 4 | 8 | 2 |
|             | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
|             | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|             | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
|             | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
|             | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
|             | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
|             | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
|             | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
|             | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
|             | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |

## Hints



$$\text{Moles of Na}_2\text{S}_2\text{O}_3 = \frac{5 \times 1}{1000} = 5 \times 10^{-3}$$

$$\text{Moles of MnO}_2 = 2.5 \times 10^{-3}$$

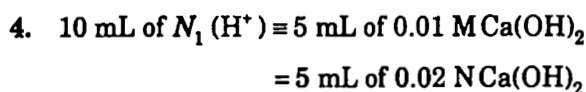
$$\text{Pure MnO}_2 = 2.5 \times 10^{-3} \text{ mol}$$

$$= 2.5 \times 10^{-3} \times 87 \text{ g}$$

$$= 0.2175 \text{ g in } 4.35 \text{ g impure}$$

sample

$$\begin{aligned} \% \text{ of pure MnO}_2 &= \frac{0.2175}{4.35} \times 100 \\ &= 5\% \end{aligned}$$



$$\therefore N_1(\text{H}^+) = 10^{-2} \text{ N}$$

$$\therefore \text{pH} = -\log [\text{H}^+] = 2$$

$$= -\log 10^{-2} = 2$$



**"A unique group of non-metals in different molecular forms.  $F_2$ ,  $Cl_2$  (gas),  $Br_2$  (liquid) and  $I_2$  (solid)."**

# 15

## Group 17 (VIIA—The Halogen Family)

### Gradation of Physical Properties

- The name halogen comes from the Greek, and means salt former. All the elements react with metals to form salts, and they are also very reactive with non-metals. Fluorine is the most reactive element known.

#### Stable isotope

| Fluorine | $^{18}F$ , $^{19}F$ (tracer)         |
|----------|--------------------------------------|
| Chlorine | $^{35}Cl$ (75%), $^{37}Cl$ (25%)     |
| Bromine  | $^{79}Br$ (50.7%), $^{81}Br$ (49.3%) |
| Iodine   | $^{127}I$                            |

- All the elements have seven electrons in their outer shell and thus complete their octet by gaining one electron (in ionic compounds as in  $NaCl$ ) or by sharing electrons (thus forming covalent bonds as in  $CCl_4$ ). Physical properties of the elements are summarised in Table 15.1 and Fig. 15.1

Physical properties like melting and boiling points are related to the size and mass of the molecules as well as intermolecular attraction. The effect of size and mass, which gradually increase as we go down the group, is easy to understand. As for the intermolecular attraction in non-polar homonuclear diatomic molecules like halogens, which do not have any permanent polarity, the only forces of attraction are the weak van der Waals' forces. The polarisability of halogens increases as we go down the group, being maximum in iodine and least in fluorine. So, van der Waals' forces of attraction are maximum in iodine and least in fluorine, with bromine and chlorine coming in between. As a consequence of this, fluorine and chlorine are gases at ordinary temperature, bromine is a liquid and iodine a solid. This is also reflected in the trends observed in their enthalpies of fusion and vaporisation.

### Learning Framework of the Chapter

- Gradation of Physical Properties
- Study of Halogens ( $X_2$ )
- Interhalogen Compounds
- Pseudohalogens and Pseudohalides
- Anomalous Behaviour of Fluorine
- Halogen Acids
- Oxoacids of Halogen
- Oxides of Halogen

$^9F$   
 $^{17}Cl$   
 $^{35}Br$   
 $^{53}I$   
 $^{85}At$



As we move along a period, the effective nuclear charge increases reaching a maximum at the noble gases. Halogens which immediately precede the noble gases have a very high effective nuclear charge coupled with small size and thus have the highest ionisation energies in the respective periods, next only to the noble gases. Like the trend in other groups, ionisation energy of halogens also decreases in going down the group from fluorine to iodine.

|    | Electrons in valence shell | Size of $X^-$ | Anion $X^-$ formation | Polarisability | van der Waals force of attraction | (EN) (EA) | BE of $X-X$ bond | Hydration energy ( $X^-$ ) | Hydration energy of $X^-$ | Size of hydrated $X^-$ | Oxidising power ( $X_2$ ) |
|----|----------------------------|---------------|-----------------------|----------------|-----------------------------------|-----------|------------------|----------------------------|---------------------------|------------------------|---------------------------|
| F  | 7                          | ↓             | ↑                     | ↓              | ↓                                 | ↑         | ↑                | ↑                          | ↑                         | ↑                      | ↑                         |
| Cl | 7                          | ↓             | ↑                     | ↓              | ↓                                 | ↑         | ↑                | ↑                          | ↑                         | ↑                      | ↑                         |
| Br | 7                          | ↓             | ↑                     | ↓              | ↓                                 | ↑         | ↑                | ↑                          | ↑                         | ↑                      | ↑                         |
| I  | 7                          | ↓             | ↑                     | ↓              | ↓                                 | ↑         | ↑                | ↑                          | ↑                         | ↑                      | ↑                         |

Larger size of anion, greater polarisability  
 EA of Cl > F  
 $F_2 < I_2 < Br_2 < Cl_2$

Halogens have seven electrons in their valence shell, they have a very strong tendency of gaining an electron to acquire a stable noble gas configuration. Therefore, they have very high electron affinities. In fact, their electron affinities are the highest in their respective periods. **Their electron affinity follows the order  $Cl > F > Br > I$ . As explained earlier, the smaller electron affinity of fluorine than that of chlorine is a consequence of its small size.**

As we go across the  $p$ -block elements in a period, the electronegativity increases reaching a maximum at the halogen group. Thus, halogens are the most electronegative elements in their respective periods. Electronegativity decreases on moving down a group, making **fluorine the most and iodine the least electronegative among the halogens.**

### DEEP Focus

In going down the group from chlorine to iodine, the  $X-X$  bond dissociation energy gradually decreases. This is easily explained by considering once again the size factor. In the chlorine molecule, which is the smallest of the three, viz.  $Cl_2$ ,  $Br_2$ ,  $I_2$ , the two bonding electrons are nearer to both the nuclei and are held strongly, while in bromine and iodine, the distance of the bonding electrons from the nuclei gradually increases resulting in lesser attraction and consequent weakening of the bond. Furthermore, as the size of the atom increases, it results in a less effective overlap of the orbitals and therefore, progressively weaker bonds are formed as we go down the group. The bond dissociation energy increases in the order  $I_2 < Br_2 < Cl_2$  and if this trend was to continue, we should expect the  $F-F$  bond dissociation energy to be greater than the bond energy of chlorine,  $210 \text{ kJ mol}^{-1}$ . But this is not so. The actual bond dissociation energy of fluorine molecule is, however, surprisingly low and has the value of  $126 \text{ kJ mol}^{-1}$  only. The anomalously low bond dissociation energy of fluorine molecule is attributed to

the fact that fluorine atom is very small and the non-bonding electrons on fluorine are nearer to each other, resulting in a much greater lone pair-lone pair repulsion, which weakens the covalent bond and lowers its dissociation energy. This repulsion is not so great in relatively larger halogen molecules like chlorine, bromine and iodine where the lone pairs are at a greater average distance from each other.

- The halogens show very close group similarities. Fluorine differs in several ways from the rest of the group due to :
  - smaller in size,
  - non availability of  $d$ -orbitals which may be used for bonding.

**Fluorine is the most reactive of all the halogens.** The difference in reactivity between fluorine and chlorine is greater than between chlorine and bromine.

- HF has a high boiling point ( $19.5^\circ\text{C}$ ) as a result of strong intermolecular hydrogen bonding, whereas all other hydrogen halides have much lower boiling point (Fig. 15.2)**

Table 15.1 Physical Properties of the Halogens

| Properties                                       | F                   | Cl                  | Br                          | I                           |
|--------------------------------------------------|---------------------|---------------------|-----------------------------|-----------------------------|
| Atomic number                                    | 9                   | 17                  | 35                          | 53                          |
| Electronic configuration                         | [He]<br>$2s^2 2p^5$ | [Ne]<br>$3s^2 3p^5$ | [Ar]<br>$3d^{10} 4s^2 4p^5$ | [Kr]<br>$4d^{10} 5s^2 5p^5$ |
| Electronegativity (Pauling)                      | 4.0                 | 3.0                 | 2.8                         | 2.5                         |
| ( $I_E$ )/ $\text{kJ mol}^{-1}$                  | 1681                | 1256                | 1143                        | 1009                        |
| EA/ $\text{kJ mol}^{-1}$                         | -333                | -349                | -325                        | -296                        |
| Hydration energy of $X^-$ / $\text{kJ mol}^{-1}$ | -515                | -381                | -347                        | -305                        |
| Atomic radius/pm                                 | 72                  | 99                  | 114                         | 133                         |
| Ionic radius( $X^-$ )/pm                         | 133                 | 184                 | 196                         | 220                         |
| Enthalpy of atomisation ( $\text{kJ mol}^{-1}$ ) | 79.1                | 122                 | 111                         | 106                         |
| $X_2 + 2e^- \rightarrow 2X^-$ $E^\circ/V$        | 2.87                | 1.40                | 1.09                        | 0.62                        |
| Bond energy ( $X-X$ )/ $\text{kJ mol}^{-1}$      | 126                 | 210                 | 158                         | 118                         |
| Melting point ( $X$ )/ $^\circ\text{C}$          | -219                | -101                | -7                          | 114                         |
| Boiling point ( $X$ )/ $^\circ\text{C}$          | -188                | -34                 | 60                          | 185                         |
| Density of solid $X_2$ (g/cc)                    | 1.3                 | 1.9                 | 3.4                         | 4.93                        |
| Oxidising power ( $X$ )                          | most                | -                   | -                           | least                       |
| Common oxidation state                           | -1                  | -1, +1, +3, +5, +7  | -1, +1, +3, +5, +7          | -1, +1, +3, +5, +7          |
| Physical form ( $X_2$ ) at room temperature      | pale yellow gas     | yellow green gas    | dark red liquid             | violet-black solid          |

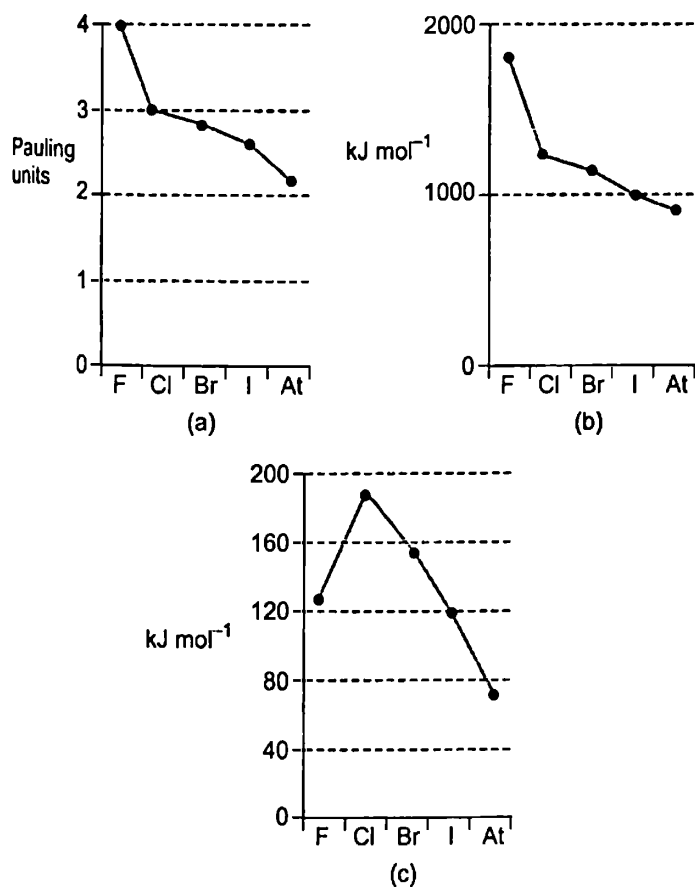
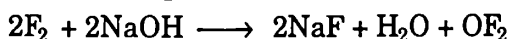


Fig. 15.1 Some group trends of the group 17 elements (a) Pauling electronegativity, (b) The first ionisation energy, and (c) Bond enthalpy in the halogens  $X_2$ .

- HF is a weak acid, whereas all other hydrohalic acids (HCl, HBr and HI) are strong acids.
- $F_2$  reacts with cold NaOH solution to produce  $OF_2$  (oxygen difluoride) gas

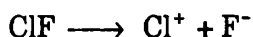


The same reaction with chlorine or bromine produces a halides ( $X^-$ ) and hypohalite ( $XO^-$ )

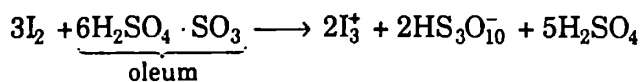
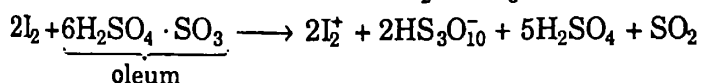


X stands for Cl or Br. Iodine ( $I_2$ ) does not react under the same condition.

- $AgF$  is soluble in water while other silver halides ( $AgCl$ ,  $AgBr$  and  $AgI$ ) are insoluble.
- Chlorine, bromine and iodine occur as halides in sea-water, and fluorine occur in the mineral fluorite ( $CaF_2$ ) and cryolite ( $Na_3AlF_6$ )
- Fluorine is the most electronegative element and has no basic properties. Chlorine shows a slight tendency to form cations.  $ClF$  ionises to form  $Cl^+$  and  $F^-$  (due to higher electronegativity of fluorine)



- Electrolysis of  $ICN$  in pyridine solution gives iodine at the cathode. This indicates that  $ICN$  ionises to give  $I^+$  and  $CN^-$ .
- Iodine dissolves in oleum giving a bright blue solution which has been shown to have  $I_2^+$  and  $I_3^-$ .



+  $SO_2$

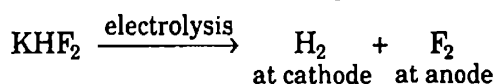
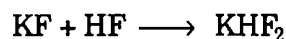
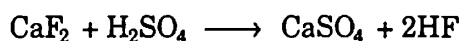
- Electrical conductivity of molten iodine is due to the presence of ( $I_2^+$  +  $I_3^-$ ) species produced by self ionisation of iodine:



## Study of Halogens ( $X_2$ )

- $F_2$  is extremely reactive, and this causes great difficulties in the preparation and handling of the element.

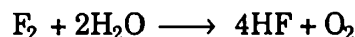
– Moissan (1886) prepared it from  $CaF_2$  :



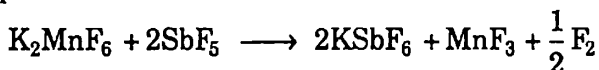
Electrodes : Pt-Ir alloy

Working temperature :  $-40^\circ C$  to  $-23^\circ C$  (using boiling  $CH_3Cl$ ,  $-23^\circ C$ )

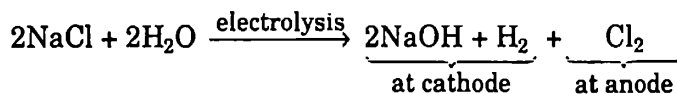
- Dennis and others (1931) also prepared  $F_2$  by using fused  $KHF_2$  with graphite electrodes in a copper vessel.
- Modern method uses graphite anode and steel cathode in a steam heated steel tank.
- If  $F_2$  were formed by the electrolysis of aqueous fluoride solution, it would immediately oxidise water to  $O_2$



Most recent method of the preparation of  $F_2$  involves reaction



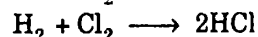
- The commercial production of  $Cl_2$  is by electrolysis, either of concentrated aqueous NaCl or of molten salt such as  $NaCl(l)$  or  $MgCl_2(l)$ :



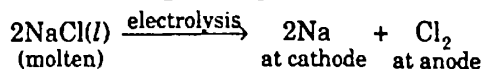
This process is called **chlor-alkali process**

### DEEP Focus

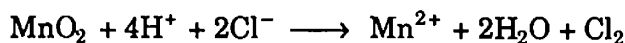
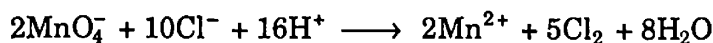
This reaction yields two useful by-products, NaOH and  $H_2$ . The cells are designed to separate the molecular chlorine from the sodium hydroxide solution and the molecular hydrogen to prevent side reactions such as



The reaction between  $H_2$  and  $Cl_2$  is explosive.

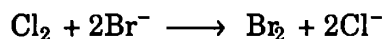


- $\text{Cl}_2$  is also prepared (in laboratory) by heating conc. HCl with  $\text{KMnO}_4$  or  $\text{MnO}_2$  (both oxidising agent):



- $\text{Br}_2$  is obtained from sea water and brine lakes. Sea water contains about 65 ppm  $\text{Br}^-$ .  $\text{Br}_2$  is isolated in following steps:

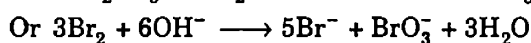
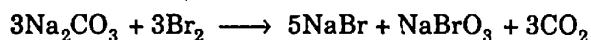
- First sea water is adjusted to pH 3.5 and treated with  $\text{Cl}_2$  which oxidises  $\text{Br}^-$  to  $\text{Br}_2$



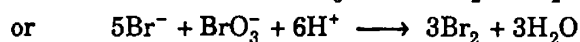
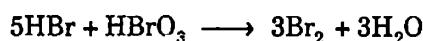
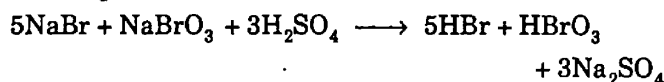
- $\text{Br}_2$  is quite volatile hence is removed by a stream of air.

### DEEP Focus

- $\text{Br}_2$  is absorbed into aqueous  $\text{Na}_2\text{CO}_3$  solution when  $\text{NaBr}$  and  $\text{NaBrO}_3$  are formed:

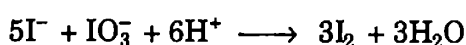
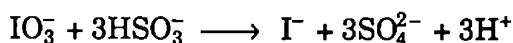


- Finally the solution is acidified and distilled to give pure  $\text{Br}_2$ :



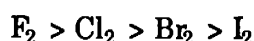
- $\text{I}_2$  is obtainable in small quantities from dried seaweed, since certain marine plants absorb and concentrate  $\text{I}^-$  selectively in presence of  $\text{Cl}^-$  and  $\text{Br}^-$ . Low concentration of  $\text{I}^-$  are also found in some natural brines (salt solutions) associated with oil fields.

**Chile saltpetre is mainly  $\text{NaNO}_3$  but it contains traces of sodium iodate  $\text{NaIO}_3$  and sodium periodate  $\text{NaIO}_4$ .  $\text{I}_2$  is recovered by reducing  $\text{IO}_3^-$  to  $\text{I}^-$  by  $\text{NaHSO}_3$  and then oxidation of  $\text{I}^-$  to  $\text{I}_2$  by  $\text{IO}_3^-$  itself:**

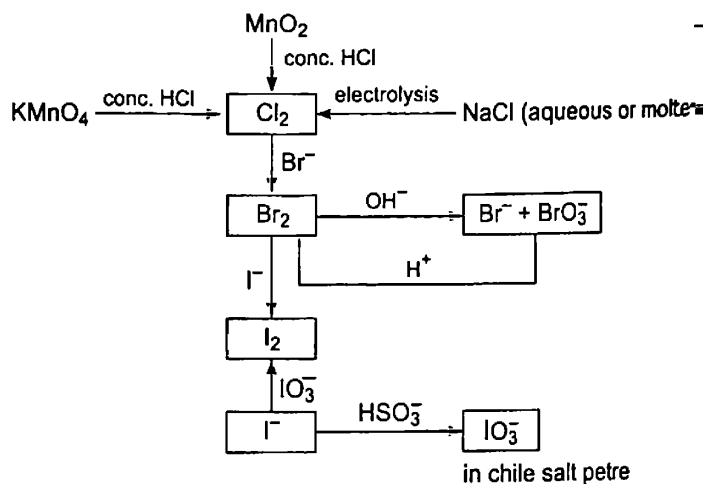


Natural brine is treated with  $\text{Cl}_2$  water to oxidise  $\text{I}^-$  to  $\text{I}_2$  and the solution is passed through an ion-exchange resin which adsorbs  $\text{I}_2$  as  $\text{I}_3^-$ .  $\text{I}_3^-$  is removed from the resin by treatment with alkali.

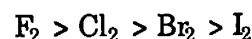
- Reactivity of halogens is based on bond-energy (BE) value:



Greater the BE, smaller the reactivity.



- Oxidising power is in order:



The oxidation potential is the energy change between the elements in its standard state, and its hydrated ions and summarised in the Table 15.2.

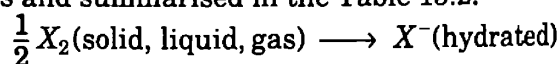
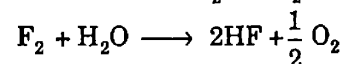


Table 15.2 Free Energy ( $\Delta G^\circ$ ) Values for  $\frac{1}{2} \text{X}_2 \longrightarrow \text{X}^-(\text{hydrated})$  (All values in  $\text{kJ mol}^{-1}$ )

|               | 1/2 Free energy of fusion | 1/2 Free energy of evaporation | 1/2 Free energy of dissociation | Electron affinity | Free energy of hydration | Sum of $\Delta G^\circ$ |
|---------------|---------------------------|--------------------------------|---------------------------------|-------------------|--------------------------|-------------------------|
| $\text{F}_2$  | —                         | —                              | 126/2                           | -333              | -460                     | -730                    |
| $\text{Cl}_2$ | —                         | —                              | 210/2                           | -349              | -348                     | -592                    |
| $\text{Br}_2$ | —                         | 31/2                           | 158/2                           | -325              | -318                     | -548.5                  |
| $\text{I}_2$  | 15/2                      | 44/2                           | 118/2                           | -296              | -279                     | -486.5                  |

### DEEP Focus

$\text{F}_2$  has the most negative  $\Delta G^\circ$  value, hence is strongest oxidising agent and can oxidise  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  to respectively  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$ .  $\text{F}_2$  can also oxidise  $\text{H}_2\text{O}$  to  $\text{O}_2$

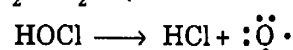
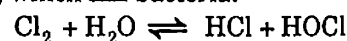


Similarly  $\text{Cl}_2$  will oxidise  $\text{Br}^-$  and  $\text{I}^-$ , and  $\text{Br}_2$  will oxidise  $\text{I}^-$ . In general any halogen ( $\text{X}_2$ ) of lower atomic number will oxidise halide ions ( $\text{X}^-$ ) of higher atomic number.

Some reactions of the halogens are summarised in Table 15.3.

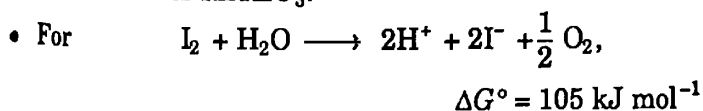
### DEEP Focus

- $\text{Cl}_2$  is used as a **bleach** or as a **disinfectant** (as in public water supplies). It reacts slowly with  $\text{H}_2\text{O}$  to form  $\text{HCl}$  and  $\text{HOCl}$ . The hypochlorous acid then decomposes into  $\text{HCl}$  and  $\text{O}$  radicals, which kill bacteria.



These oxygen radicals are very strong oxidising as well as effective bleaching and disinfecting agent in aqueous solution of  $\text{Cl}_2$  or hypochlorite salts.

• Iodine is necessary for the normal functioning of the thyroid gland. Insufficient iodine in the diet leads to Goitre (enlargement of the thyroid gland) 'Iodised salt' contains KI/KIO<sub>3</sub>.



and thus for reverse reaction  $\Delta G^\circ = -105 \text{ kJ mol}^{-1}$ , hence reverse reaction occurs spontaneously and even atmospheric O<sub>2</sub> oxidises I<sup>-</sup> to I<sub>2</sub>.

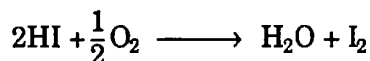


Table 15.3 Some Reactions of Halogen

| Reaction                                                                                                                                                                                                                                                                                                                                                                       | Comment                                                                                                                                                                                                                                |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>• With H<sub>2</sub>O</p> $2\text{F}_2 + 2\text{H}_2\text{O} \longrightarrow 4\text{H}^+ + 4\text{F}^- + \text{O}_2$ $2\text{X}_2 + 2\text{H}_2\text{O} \longrightarrow 4\text{H}^+ + 4\text{X}^- + \text{O}_2$ $\text{X}_2 + \text{H}_2\text{O} \xrightarrow{\text{disproportionate}} \text{X}^- + \text{HOX} + \text{H}^+$                                                | Vigorous reaction with F <sub>2</sub> ; atmospheric O <sub>2</sub> can oxidise I <sup>-</sup> to I <sub>2</sub> hence, reverse reaction Cl <sub>2</sub> > Br <sub>2</sub> > I <sub>2</sub> (F <sub>2</sub> does not disproportionate). |
| <p>• With H<sub>2</sub></p> $\text{H}_2 + \text{X}_2 \longrightarrow 2\text{HX}$                                                                                                                                                                                                                                                                                               | All the halogens, with Br <sub>2</sub> photochemical reaction, with I <sub>2</sub> very slow even at high temperature.                                                                                                                 |
| <p>• With metals</p> $2\text{M} + n\text{X}_2 \longrightarrow 2\text{MX}_n$                                                                                                                                                                                                                                                                                                    | Most metals form halides.                                                                                                                                                                                                              |
| <p>• With CO</p> $\text{CO} + \text{X}_2 \longrightarrow \text{COX}_2$                                                                                                                                                                                                                                                                                                         | Only Cl <sub>2</sub> , Br <sub>2</sub> form carbonyl halide                                                                                                                                                                            |
| <p>• With P</p> $2\text{P} + 3\text{X}_2 \longrightarrow 2\text{PX}_3$ $2\text{P} + 5\text{X}_2 \longrightarrow 2\text{PX}_5$                                                                                                                                                                                                                                                  | For F, Cl, Br, I<br>For F, Cl, Br                                                                                                                                                                                                      |
| <p>• With S</p> $2\text{S} + \text{X}_2 \longrightarrow \text{S}_2\text{X}_2$ $\text{S} + 2\text{Cl}_2 \longrightarrow \text{SCl}_4$ $\text{S} + 3\text{F}_2 \longrightarrow \text{SF}_6$                                                                                                                                                                                      | Cl, Br                                                                                                                                                                                                                                 |
| <p>• With H<sub>2</sub>S</p> $\text{H}_2\text{S} + \text{X}_2 \longrightarrow 2\text{HX} + \text{S}$                                                                                                                                                                                                                                                                           | All the halogens oxidise H <sub>2</sub> S (S <sup>2-</sup> ) to S                                                                                                                                                                      |
| <p>• With SO<sub>2</sub></p> $\text{SO}_2 + \text{X}_2 \longrightarrow \text{SO}_2\text{X}_2$                                                                                                                                                                                                                                                                                  | F and Cl                                                                                                                                                                                                                               |
| <p>• With NH<sub>3</sub></p> $8\text{NH}_3 + 3\text{X}_2 \longrightarrow \text{N}_2 + 6\text{NH}_4\text{X}$                                                                                                                                                                                                                                                                    | F, Cl, Br                                                                                                                                                                                                                              |
| <p>• With halogens</p> $\text{X}_2 + \text{X}'_2 \longrightarrow 2\text{XX}'$                                                                                                                                                                                                                                                                                                  | Interhalogen compounds                                                                                                                                                                                                                 |
| <p>• With cold NaOH</p> $2\text{NaOH} + 2\text{F}_2 \longrightarrow 2\text{NaF} + \text{OF}_2 + \text{H}_2\text{O}$ $2\text{NaOH} + \text{X}_2 \longrightarrow \text{NaX} + \text{NaOX} + \text{H}_2\text{O}$ <p>Cl<sub>2</sub> reacts with dry slaked lime forming bleaching powder</p> $\text{Ca(OH)}_2 + \text{Cl}_2 \longrightarrow \text{CaCl(OCl)} + \text{H}_2\text{O}$ | (X = Cl, Br) I <sub>2</sub> does not react under the same condition.                                                                                                                                                                   |
| <p>• With hot NaOH</p> $6\text{NaOH} + 3\text{X}_2 \longrightarrow 5\text{NaX} + \text{NaXO}_3 + 3\text{H}_2\text{O}$                                                                                                                                                                                                                                                          | (X = Cl, Br, I)                                                                                                                                                                                                                        |

## Colour of Halogens

In gaseous phase, colours of the halogens vary remarkably :

F<sub>2</sub> — pale yellow

Cl<sub>2</sub> — pale greenish yellow

Br<sub>2</sub> — deep red-brown

I<sub>2</sub> — deep violet

All these colours may be assigned to transition of an electron from the highest occupied π\* molecular orbital to the lowest occupied σ\* molecular orbital. As one moves from F<sub>2</sub> to I<sub>2</sub>, the difference between the two energy levels decreases and probability of this transition also increases at the same time. Hence, the absorption maximum gradually shifts from the near UV to the red region of the

visible spectrum; the intensity of absorption also increases side by side. Hence, we observe the complimentary colour with increasing intensity.

## Interhalogen Compounds

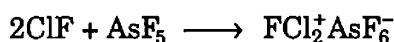
- The halogens react with each other to form **interhalogen compounds** of the type  $AX$ ,  $AX_3$ ,  $AX_5$  and  $AX_7$  of which  $A$  is of higher atomic number as shown :

| $AX$ | $AX_3$                                             | $AX_5$           | $AX_7$          |
|------|----------------------------------------------------|------------------|-----------------|
| ClF  | ClF <sub>3</sub>                                   | ClF <sub>5</sub> |                 |
| BrF  | BrF <sub>3</sub>                                   | BrF <sub>5</sub> |                 |
| ICl  | ICl <sub>3</sub> (I <sub>2</sub> Cl <sub>6</sub> ) | IF <sub>5</sub>  | IF <sub>7</sub> |
| IBr  |                                                    |                  |                 |
| BrCl |                                                    |                  |                 |

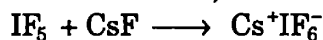
- There are never more than two different halogens in a molecule. The bonds are covalent because of the small electronegativity difference. Ternary combinations occur in polyhalide ions (*e.g.*,  $\text{IBrCl}^-$ )

– Neutral interhalogen compounds are of the type  $AX_n$  where  $n$  is an odd number and  $X$  is always lighter halogen when  $n > 1$ . Because  $n$  is odd the compounds are diamagnetic, their valence electrons are present as bonding pairs or as unshared pairs.

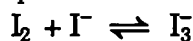
– Interhalogen ions can be either cations or anions. Halogen fluorides react with fluoride ion acceptors,



or with fluoride ion donors,

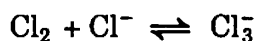


– The pale yellow triiodide ion ( $\text{I}_3^-$ ) is formed by dissolving  $\text{I}_2$  in aqueous KI.



Other ions are not usually stable in aqueous solution although they can be obtained in  $\text{CH}_3\text{OH}$  or  $\text{CH}_3\text{CN}$  and as crystalline salts of large cations as  $\text{Cs}^+$  or  $\text{R}_4\text{N}^+$ .

$\text{Cl}_3^-$  is formed only in concentrated solution

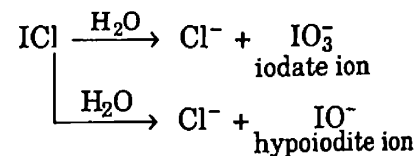
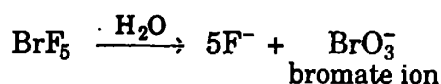


– The electrical conductance of molten  $\text{I}_2$  is ascribed to self-ionisation

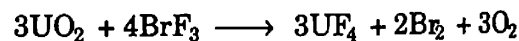


– The interhalogens are generally more reactive than the halogens (except  $\text{F}_2$ ). This is because the  $A-X$  bond in interhalogens is weaker than the  $X-X$  bond in the halogens.

– Hydrolysis of interhalogens gives halide and oxohalide. **Oxohalide is always formed from larger halogens present :**



– Interhalogen compounds can fluorinate many metal oxides, metal halides and metals :



Some interhalogen compounds are summarised below in Table 15.4

Table 15.4 Interhalogen Compounds and their Properties

| Type of inter-halogen compound | Formulae and names of compounds            | Physical state and colour at ordinary temperatures | Melting point (K) | Boiling point (K) |
|--------------------------------|--------------------------------------------|----------------------------------------------------|-------------------|-------------------|
| $XY$                           | ClF<br>Chlorine fluoride                   | Gas, colourless                                    | 119               | 163               |
|                                | BrF<br>Bromine fluoride                    | Liquid below 293 K, Pale-brown gas above 293 K     | 240               | 293               |
|                                | BrCl<br>Bromine chloride                   | Liquid, reddish yellow                             | 207               | 283               |
|                                | ICl<br>Iodine chloride                     | Solid, rubby red                                   | —                 | 310               |
|                                | IBr<br>Iodine bromide                      | Solid, brown like iodine                           | 232               | —                 |
| $XY_3$                         | ClF <sub>3</sub><br>Chlorine trifluoride   | Liquid below 261 K, colourless gas above 261 K     | 197               | 261               |
|                                | BrF <sub>3</sub><br>Bromine trifluoride    | Liquid, colourless                                 | 282               | 400               |
|                                | BrCl <sub>3</sub><br>Bromine trichloride   | Solid, orange                                      | 374 (decomposes)  | —                 |
| $XY_5$                         | ClF <sub>5</sub><br>Chlorine pentafluoride | Gas, colourless                                    | 170               | 259               |
|                                | BrF <sub>5</sub><br>Bromine pentafluoride  | Liquid colourless                                  | 213               | 314               |
|                                | IF <sub>5</sub><br>Bromine pentafluoride   | Liquid colourless                                  | 283               | 314               |
| $XY_7$                         | IF <sub>7</sub><br>Iodine heptafluoride    | Gas, colourless                                    | 279.5             | —                 |

## Structure of Interhalogen Compounds

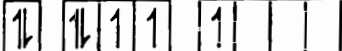
The interhalogen compounds are generally covalent in which the larger atom lies in the centre. Their shapes can be predicted by VSEPR theory (Chapter 7) Shapes of some of the interhalogen compounds are given below

| Molecule        | Total number of electron pairs around X | Bond pairs | Lone pairs | Shape                  |
|-----------------|-----------------------------------------|------------|------------|------------------------|
| XY              | 4                                       | 1          | 3          | Linear                 |
| XY <sub>3</sub> | 5                                       | 3          | 2          | T-shaped               |
| XY <sub>5</sub> | 6                                       | 5          | 1          | Square pyramidal       |
| XY <sub>7</sub> | 7                                       | 7          | 0          | Pentagonal bipyramidal |

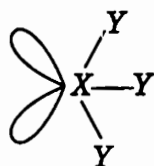
Structure of interhalogens can be explained with the help of Valence Bond Theory also in the following manner :

(i) **Type XY** As expected, the compounds of the type XY are linear. Thus, ClF, BrF, BrCl, IBr and ICl all have a linear structure. In these compounds both the halogen atoms have an unpaired electron in the  $p_z$  orbital. Axial overlap of the  $p_z$  orbitals of the two halogen atoms results in a **linear interhalogen molecule**.

(ii) **Type XY<sub>3</sub>** Structure of the interhalogens of this type can be explained on the basis of  $sp^3d$  hybridisation of the central halogen atom X. Three of the hybrid orbitals having an electron each are used in making three covalent bonds with three atoms of the other halogen atom. The remaining two orbitals accommodate the two lone pairs of the central atom. In order to minimise lone pair-lone pair and lone pair-bond pair repulsions, the lone pairs occupy the two equatorial sites around the central halogen atom, thereby giving a T-shape to the molecule. Thus, ClF<sub>3</sub>, BrF<sub>3</sub> and ICl<sub>3</sub> have a **T-shaped structure**.

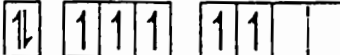
X atom in excited state 

$sp^3d$  hybridisation-trigonal bipyramidal structure with two equatorial sites occupied by lone pairs



T-shaped structure of interhalogen molecules of the types XY<sub>3</sub>

(iii) **Type XY<sub>5</sub>** This type of compounds have a square pyramidal structure (instead of octahedral due to VSEPR). The central atom X uses five of its seven valence electrons in forming five bonds with Y and two electrons remains as a lone pair. Thus, X-atom in XY<sub>5</sub> molecule is  $sp^3d^2$  hybridised. The lone pair occupies the axial hybrid orbital.

X atom in excited state 

$sp^3d^2$  hybridisation-octahedral structure with one of the axial sites occupied by lone pair

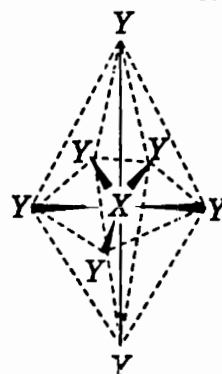


Square pyramidal structure of interhalogen molecules of the type XY<sub>5</sub>

(iv) **Type XY<sub>7</sub>** In these molecules, the central X atom uses all its seven valence electrons in forming seven X—Y bonds. Formation of this type of compounds can be explained on the basis of  $sp^3d^3$  hybridisation of the X atom. These compounds have a pentagonal bipyramidal structure with two axial X—Y bonds and five equatorial X—Y bonds. Bond angle is 72° for five  $sp^3d^3$  orbitals and other two are at 90° with first the  $sp^3d^3$  orbitals.

X atom in excited state 

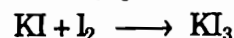
$sp^3d^3$  hybridisation-pentagonal bipyramidal structure



Pentagonal bipyramidal structure of interhalogen molecules of the type XY<sub>7</sub>

## Polyhalides and Polyhalonium Ions

Halide ions often associate with molecules of halogens or with interhalogen compounds to form polyhalide ions. For example, on addition of potassium iodide, the solubility of iodine in water is greatly enhanced due to the formation of the triiodide ion, I<sub>3</sub><sup>-</sup> :



More complex ions of iodine, such as pentaiodide, I<sub>5</sub><sup>-</sup>, heptaoidide, I<sub>7</sub><sup>-</sup> and noniodide, I<sub>9</sub><sup>-</sup> are also known.

These are generally found in the form of salts of large metal ions, as Rb<sup>+</sup>I<sub>5</sub><sup>-</sup> · 2C<sub>6</sub>H<sub>6</sub> or large complex cations, as NH<sub>4</sub><sup>+</sup>I<sub>5</sub><sup>-</sup>, (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N<sup>+</sup>I<sub>7</sub><sup>-</sup>. A number of mixed polyhalide ions containing two or three different halogens are also known, as ICl<sub>2</sub><sup>-</sup>, ICl<sub>4</sub><sup>-</sup> and IBrF<sup>-</sup> and IBrCl<sup>-</sup>.

All the polyhalides are hydrolysed to some extent in aqueous solution. The ease of hydrolysis increases with the introduction of the more electronegative halogen, into the ion. Thus, the triiodide being the most stable and  $\text{Cl}_3^-$  the least. In non-aqueous solutions, polyhalides behave as mild halogenating agents.

Polyhalonium cations, e.g.,  $\text{ICl}_4^+$  and  $\text{BrF}_2^+$  are formed as a result of autoionisation of  $\text{ICl}_3$  and  $\text{BrF}_3$ . Other cations like  $\text{Br}_2^+$ ,  $\text{I}_2^+$ ,  $\text{I}_3^+$ ,  $\text{ClF}_2^+$ ,  $\text{IF}_2^+$ ,  $\text{IBr}_2^+$ ,  $\text{IBrCl}^+$ ,  $\text{ClF}_4^+$ ,  $\text{BrF}_4^+$ ,  $\text{IF}_4^+$ ,  $\text{ClF}_6^+$ ,  $\text{BrF}_6^+$ ,  $\text{IF}_6^+$ , etc. are also known. These are stabilised by large anions like  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{AlCl}_4^-$ ,  $\text{SbCl}_6^-$ , etc.

## Pseudohalogens and Pseudohalides

Some molecules like cyanogen,  $(\text{CN})_2$ , thiocyanogen,  $(\text{SCN})_2$  and selenocyanogen,  $(\text{SeCN})_2$ , have properties similar to those of the halogens. Therefore, these are called pseudohalogens. Pseudohalogens form hydro acids similar to the hydrohalic acids, e.g.,  $\text{H—CN}$ . They also form anions such as cyanide,  $\text{CN}^-$ , cyanate,  $\text{OCN}^-$ , thiocyanate,  $\text{SCN}^-$ , selenocyanate,  $\text{SeCN}^-$ , tellurocyanate,  $\text{TeCN}^-$  and azide,  $\text{N}_3^-$ , which resemble the halide ions to some extent.

### DEEP Focus

The best known pseudohalide is the cyanide,  $\text{CN}^-$ , which resembles  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  in the following respects :

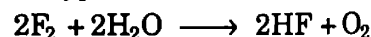
- It can be oxidised to form a molecule,  $(\text{CN})_2$ .
- It forms an acid  $\text{HCN}$  similar to  $\text{HCl}$ ,  $\text{HBr}$ , etc.
- It forms insoluble salts with  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^+$ .
- Interpseudohalogen compounds  $\text{ClCN}$ ,  $\text{BrCN}$  and  $\text{ICN}$  can also be formed.
- Like  $\text{AgCl}$ ,  $\text{AgCN}$  is insoluble in water but soluble in liquor ammonia.
- It forms a large number of complexes similar to the halide complexes, e.g.,  $[\text{Cu}(\text{CN})_4]^{2-}$  is similar to  $[\text{CuCl}_4]^{2-}$  and  $[\text{Co}(\text{CN})_6]^{3-}$  is similar to  $[\text{CoCl}_6]^{3-}$ .

## Anomalous Behaviour of Fluorine

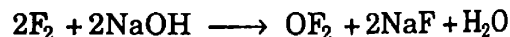
Fluorine differs from other elements of the group because of its exceptionally small atomic and ionic size and low fluorine—fluorine bond dissociation energy. The result of these differences is that fluorine is the most electronegative element in the Periodic Table and is a powerful oxidant. Some difference between fluorine and other halogens are :

- It is more reactive than other halogens because of low  $\text{F—F}$  bond energy, also due to its high electronegativity the bond between fluorine and other elements is very strong so its compounds are more stable. Some of them are inert, e.g.,  $\text{SF}_6$ .
- Fluorine is almost invariably monocoordinate (coordination number = 1) and is never more than monocovalent.
- Fluorides are more ionic.
- Fluorine forms strong hydrogen bonds resulting in the properties of hydrogen fluoride being anomalous.

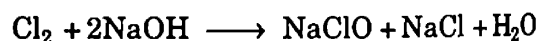
- Fluorine is the strongest oxidising agent and oxidises the elements to their highest oxidation state, for example in  $\text{IF}_7$ , iodine has oxidation number seven.
- The reactions of fluorine are also different from other halogens. Fluorine fumes in moist air and decomposes water to give oxygen, whereas other halogens are sparingly soluble in water and react partly to give hydrohalic and hypohalous acids.



Fluorine reacts with alkalis to yield the oxide,  $\text{OF}_2$ .



The other halogens react with alkalis to yield a solution of hypohalite ions, which may disproportionate. The oxoacid of fluorine,  $\text{HOF}$ , prepared recently is very unstable. The oxides of fluorine are not acidic.

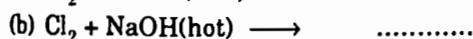
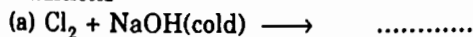


## Uses of Halogens

| Halogen       | Uses                                                                               | Remark                                                                                                                                                                                   |
|---------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\text{F}_2$  | In the preparation of $\text{UF}_6$                                                | $\text{UF}_6$ used in the gaseous diffusion process for separating isotopes of uranium ( $\text{U-235}$ and $\text{U-238}$ )                                                             |
|               | In the preparation of teflon $-(\text{CF}_2-\text{CF}_2)_n$                        | Teflon is used in electrical insulators, high temperature plastic and cooking utensils                                                                                                   |
| $\text{Cl}_2$ | $\text{Cl}^-$ ion is the principal anion in intracellular and extracellular fluids | —                                                                                                                                                                                        |
|               | $\text{Cl}_2$ as bleaching agent                                                   | Household laundry bleach contains the active ingredient $\text{NaOCl}$ (sodium hypochlorite) about 5% by mass)                                                                           |
|               | $\text{Cl}_2$ used to purify water (as disinfectant)                               | $\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \text{HCl} + \text{HOCl}$<br>$\text{ClO}^-$ ions destroy bacteria by oxidising life-sustaining compounds within them                   |
|               | As a chlorinating agent to prepare various organic compounds                       | $\text{CHCl}_3$ , $\text{CCl}_4$ , $\text{CH}_2=\text{CHCl}$ , $\text{BHC}$ , $\text{DDT}$                                                                                               |
| $\text{Br}_2$ | To prepare ethylene dibromide $\text{BrCH}_2\text{CH}_2\text{Br}$                  | $\text{BrCH}_2\text{CH}_2\text{Br}$ is used as an insecticide and as a scavenger for lead in gasoline to keep lead deposits from clogging engines                                        |
|               | To prepare $\text{AgBr}$                                                           | $\text{AgBr}$ is used in photographic plate                                                                                                                                              |
| $\text{I}_2$  | To prepare tincture of iodine—an antiseptic                                        | 50% (by mass) alcohol solution of iodine is called tincture of iodine                                                                                                                    |
|               | In iodised salt                                                                    | Iodised salt contains 0.01 per cent $\text{KI}$ or $\text{NaI}$ which is more than sufficient to satisfy 1 mg iodine per week required for the formation of thyroxine in the human body. |
|               | To prepare $\text{AgI}$                                                            | Used in cloud seeding—process for inducing rainfall.                                                                                                                                     |

## Target Practice 1

1.  $\text{Cl}_2$  gas is passed aqueous  $\text{NaOH}$  solution under given conditions



Write balanced ionic reactions

Equivalent mass of  $\text{Cl}_2$  in (a) is  $\dots\dots\dots$

Equivalent mass of  $\text{Cl}_2$  in (b) is  $\dots\dots\dots$

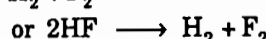
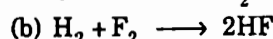
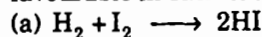
2. (a)  $(\text{CN})_2$  cyanogen is also called  $\dots\dots\dots$   
 (b)  $\text{CN}^-$  cyanide ion is also called  $\dots\dots\dots$   
 (c) Bond energy of  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$  in increasing order is  $\dots\dots\dots$   
 (d) Electron-affinity is maximum (out of F, Cl Br and I) for  $\dots\dots\dots$   
 (e)  $\text{OF}_2$  is formed by the reaction  $\dots\dots\dots$

3.  $\Delta G_f^\circ$  (standard free energy of formation) of

$$\text{HF}(g) = -273.20 \text{ kJ mol}^{-1}$$

$$\text{HI}(g) = +1.72 \text{ kJ mol}^{-1}$$

Based on the above data, select which reaction is most favourable in each case



4. Out of HF, HCl, HBr and HI, select

(a) strongest acid  $\dots\dots\dots$

(b) weaker acid  $\dots\dots\dots$

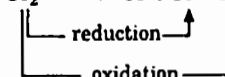
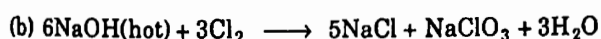
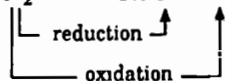
(c) acid with maximum boiling point  $\dots\dots\dots$

(d) acid that attacks glass  $\dots\dots\dots$

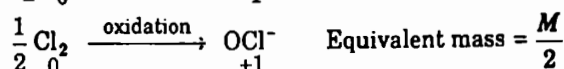
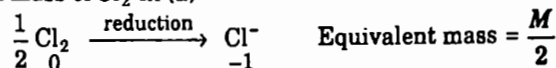
(e) acid with maximum dipole moment  $\dots\dots\dots$

(f) acid which has been used as non-aqueous solvent  $\dots\dots\dots$

## Answers



Equivalent mass of  $\text{Cl}_2$  in (a)

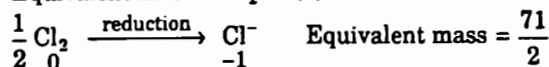


Net equivalent mass = in reduction part + in oxidation part

$$= \frac{M}{2} + \frac{M}{2} = M$$

$$= 71.0 \text{ g equivalent}^{-1}$$

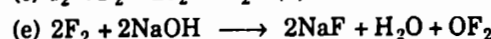
Equivalent mass of  $\text{Cl}_2$  in (b)



$$\therefore \text{Net equivalent mass} = \frac{71}{2} + \frac{71}{10} = 42.6 \text{ g equivalent}^{-1}$$

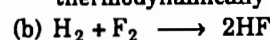
2. (a) Pseudohalogen (b) Pseudohalide

(c)  $\text{I}_2 < \text{F}_2 < \text{Br}_2 < \text{Cl}_2$  (d) Cl



3. (a)  $\text{H}_2 + \text{I}_2 \longrightarrow 2\text{HI}$   $\Delta G_f^\circ = +ve$

Decomposition of HI is kinetically controlled. (rather than thermodynamically controlled)



Very fast since,  $\Delta G_f^\circ = -ve$

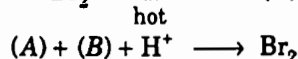
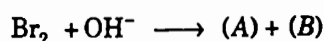
4. (a) HI (b) HF (c) HF (d) HF (e) HF (f) HF

## Practice Exercise 1

1. (a)  $\text{ICl}$  is found to be partially ionised in fused state. Give reaction.

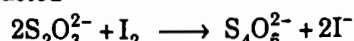
(b)  $\text{ICl}$  is also found to form addition compound with  $\text{NaBr}$  and  $\text{KI}$ . Write the formulae of the addition compounds.

2. Identify (A) and (B).



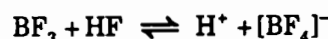
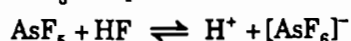
(A) gives yellow ppt with  $\text{AgNO}_3$ .

3. When  $\text{I}_2$  is estimated by  $\text{Na}_2\text{S}_2\text{O}_3$  iodometrically, blue colour (due to starch) changes to colourless when  $\text{I}_2$  has completely reacted



but after sometimes blue colour reappears. Explain

4.  $\text{SbF}_5$ ,  $\text{AsF}_5$  and  $\text{BF}_3$  accept  $\text{F}^-$  from  $\text{HF}$  as :

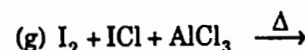
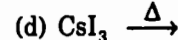
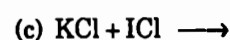
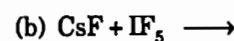
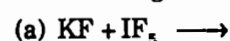


Identify nature of HF and fluorides.

5.  $\text{CN}^-$  resembles  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  in many of its properties. What is it called ? Give some other examples which resemble halides.

6. Select the species which are soluble in  $\text{H}_2\text{O}$  and which are soluble in  $\text{NH}_3(aq)$   $\text{AgF}$ ,  $\text{AgCN}$ ,  $\text{AgCl}$ ,  $\text{AgI}$ ,  $\text{CaF}_2$ ,  $\text{CaCl}_2$ .

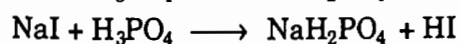
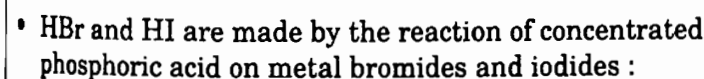
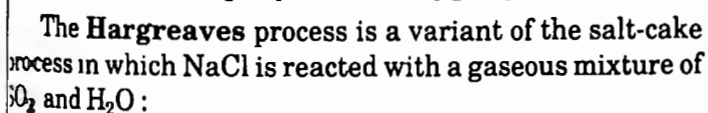
7. Identify the products (which can be in the form of ions) in the following :







NaCl is now replaced by  $\text{NH}_4\text{Cl}$  since  $\text{NH}_4\text{HSO}_4$  (intermediate) is water soluble and reaction goes to completion:



Concentrated  $\text{H}_2\text{SO}_4$  (a strong oxidising agent) can't be used since it would oxidise  $\text{HBr}$  to  $\text{Br}_2$  and  $\text{HI}$  to  $\text{I}_2$ .

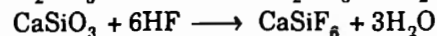
$$2\text{P}_{\text{red}} + 3\text{Br}_2 \longrightarrow 2\text{PBr}_3$$


Boiling point  $\text{HCl} < \text{HBr} < \text{HI} < \text{HF}$

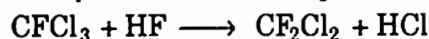


## DEEP Focus

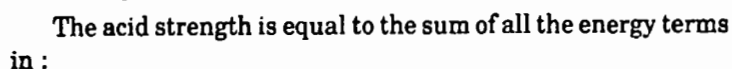
- HF attacks glass, other halogen acids do not. Glass is silicates of sodium and calcium and are converted into complex fluorides :



- HF also reacts with  $\text{CCl}_4$  to form **freons** (refrigerant)


$$\begin{array}{ccccccc} \text{H}_2\text{O} & + & \text{HX}^- & \rightleftharpoons & \text{H}_3\text{O}^+ & + & \text{X}^- \\ \text{base} & & \text{acid} & & \text{acid} & & \text{base} \end{array}$$
$$\text{HF} \quad \underbrace{< \text{HCl} < \text{HBr} < \text{HI}}_{\text{strong}}$$

Acid strength is dependent not on the electronegativity difference of H and X but on the tendency of the hydrated molecule to form hydrogen ions :

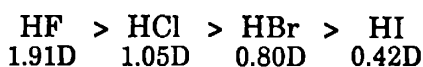

$$\text{HLX (hydrated)} \longrightarrow \text{H}^+ \text{ (hydrated)} + \text{X}^- \text{ (hydrated)}$$

$$\Delta H = x_1 + x_2 + x_3 + x_4 + x_5$$

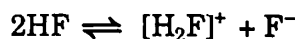
$$\Delta G_f^\circ \text{ HI} < \text{HBr} < \text{HCl} < \text{HF}$$

+ve
-ve

- Dipole moment of HF is maximum and is in order

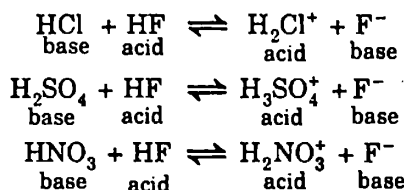


- Liquid HF has been used as a non-aqueous solvent. It undergoes self ionisation.

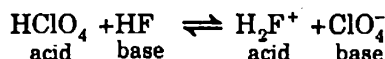


### DEEP Focus

Acid-base reactions occur in this solvent system. However, the solvent itself has a very strong tendency to donate protons. Mineral acids like  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$ , when dissolved in HF, behave as bases in HF as they accept proton from HF :



$\text{HClO}_4$  (perchloric acid) however behaves as an acid in liquid HF which acts like a base :



## Oxoacids of Halogen

Five series of oxoacids are known and are summarised in Table 15.5.

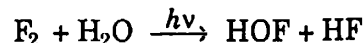
Table 15.5 Oxoacids of Halogen

|                      | HOX<br>hypohalous acid        | HXO <sub>2</sub><br>halous acid             | HXO <sub>3</sub><br>halic acid                         | HXO <sub>4</sub><br>perhalic acid               | H <sub>5</sub> XO <sub>6</sub><br>para perhalic acid |
|----------------------|-------------------------------|---------------------------------------------|--------------------------------------------------------|-------------------------------------------------|------------------------------------------------------|
|                      | HOF                           | —                                           | —                                                      | —                                               | —                                                    |
|                      | HOCl                          | HClO <sub>2</sub>                           | HClO <sub>3</sub>                                      | HClO <sub>4</sub>                               | —                                                    |
|                      | HOBr                          | —                                           | HBrO <sub>3</sub>                                      | HBrO <sub>4</sub>                               | —                                                    |
|                      | HOI                           | —                                           | HIO <sub>3</sub>                                       | HIO <sub>4</sub>                                | H <sub>5</sub> IO <sub>6</sub>                       |
| Anhydride            | X <sub>2</sub> O              | X <sub>2</sub> O <sub>3</sub>               | X <sub>2</sub> O <sub>5</sub>                          | X <sub>2</sub> O <sub>7</sub>                   | I <sub>2</sub> O <sub>7</sub>                        |
| Oxidation state of X | +I                            | +III                                        | +V                                                     | +VII                                            | +VII                                                 |
| Oxidising power      | strong                        | ←————→                                      | ————→                                                  | weak                                            |                                                      |
| Acid strength*       | weak                          | ————→                                       | ————→                                                  | strong                                          |                                                      |
| Thermal stability    | weak                          | ————→                                       | ————→                                                  | good                                            |                                                      |
| Hydrolysis of anion  | max                           | ←————→                                      | ————→                                                  | min                                             |                                                      |
| Structure of anion   | (OCI <sup>-</sup> )<br>linear | (ClO <sub>2</sub> <sup>-</sup> )<br>angular | (ClO <sub>3</sub> <sup>-</sup> )<br>trigonal pyramidal | (ClO <sub>4</sub> <sup>-</sup> )<br>tetrahedral |                                                      |

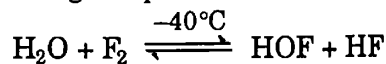
\*Acid strength of one type oxoacid increases as size of halogen atom increases

## HOX series

- +I oxidation state in HOF appears very doubtful but this has been prepared by trapping  $\text{F}_2$  and  $\text{H}_2\text{O}$  in a unreactive matrix of solid  $\text{N}_2$  (at very low temperature) and photolysing the gases :

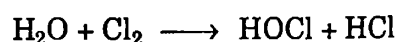


It has been recently prepared by passing  $\text{F}_2$  over ice at  $0^\circ\text{C}$  and removing the product into a cold trap:



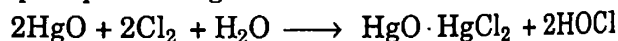
HOCl, HOBr and HOI are not very stable and are known only in aqueous solution.

- HOCl is formed when  $\text{Cl}_2$  is dissolved in  $\text{H}_2\text{O}$ .  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$  all dissolve to some extent in water forming hydrated  $\text{X}_2$  molecules, and  $\text{X}^-$  and  $\text{OX}^-$  ions :

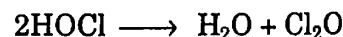


(Bleaching action of chlorine water is due to formation of HOCl)

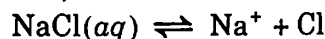
- HOX are also formed by shaking  $\text{X}_2$  with freshly precipitated  $\text{HgO}$  in water :



The solution, after filtration, is distilled whereby the dilute acid passes over. The maximum concentration which can be obtained is only 25 per cent. In the process of distillation, the acid decomposes into its anhydride,  $\text{Cl}_2\text{O}$ .

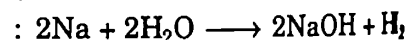
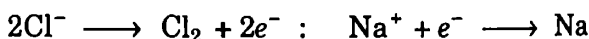


- Salts of HOX are called **hypohalites** and are bleaching agent. NaOCl is formed due to electrolysis of cold NaCl (brine) solution :

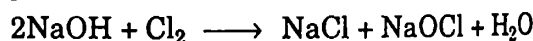


at anode :

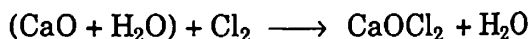
at cathode :



If anode and cathode are not separated, NaOH and  $\text{Cl}_2$  mix forming NaOCl.

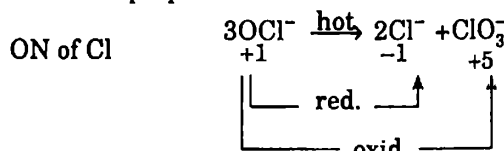


\* Bleaching powder  $\text{CaOCl}_2$  is formed when  $\text{Cl}_2$  is passed into moist lime  $\text{CaO}$ .  $\text{CaOCl}_2$  has  $\text{Ca}^{2+}$ ,  $\text{OCl}^-$  and  $\text{Cl}^-$  ions

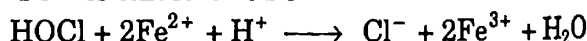


### DEEP Focus

- $\text{OCl}^-$  disproportionates in hot solution



- $\text{Fe}^{2+}$  is oxidised to  $\text{Fe}^{3+}$

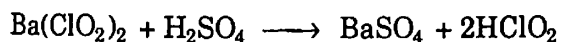


\*  $\text{OCl}^-$  also oxidises  $\text{I}^-$  to  $\text{I}_2$  in acidic medium.

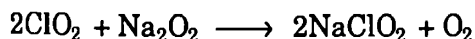


### $\text{HXO}_2$ series

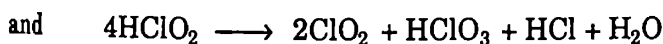
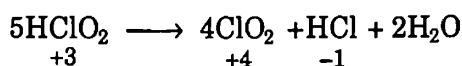
- Only stable acid known is  $\text{HClO}_2$  and exists in solution :



- Salts are called **chlorites** and are made from :

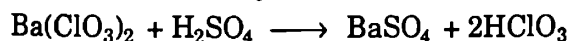


- It is stable in alkaline solution but disproportionates in acid solution :

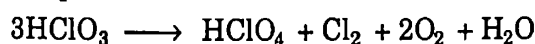


### $\text{HXO}_3$ series

- $\text{HClO}_3$ ,  $\text{HBrO}_3$ ,  $\text{HIO}_3$  are known of which most stable is  $\text{HIO}_3$ . Salts like  $\text{NaClO}_3$ ,  $\text{NaBrO}_3$ ,  $\text{NaIO}_3$  are stable :

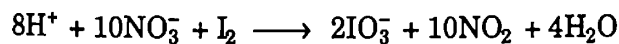


After reaction,  $\text{BaSO}_4$  is removed by filtration, and the filtrate is evaporated in vacuum till 40 per cent solution is obtained. However, further concentration by evaporation leads to decomposition :



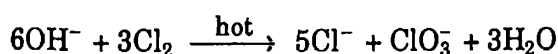
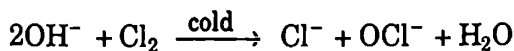
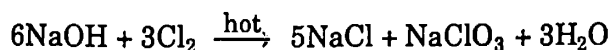
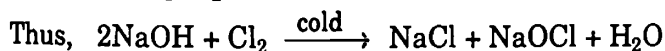
Similarly for  $\text{HBrO}_3$ .

$\text{HIO}_3$  is formed by oxidation of  $\text{I}_2$  with concentrated  $\text{HNO}_3$  or  $\text{O}_3$ .



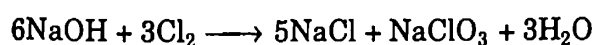
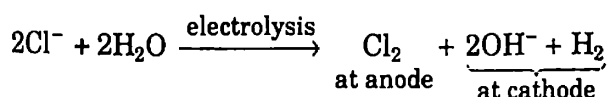
Chlorates, etc. may be made :

- by passing  $\text{Cl}_2$  into hot alkali solution.

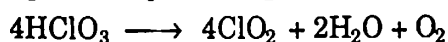


In this  $\text{Cl}_2$  undergoes disproportionation.

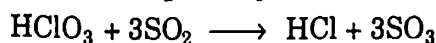
- by electrolysis of hot halide solutions (with vigorous stirring)



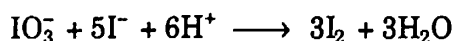
- $\text{HClO}_3$  on evaporation gives  $\text{ClO}_2$  :



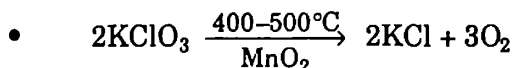
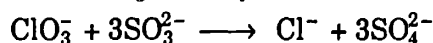
- $\text{HClO}_3$  oxidises  $\text{SO}_2$  to  $\text{SO}_3$



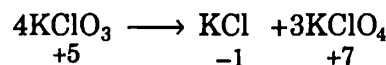
- $\text{IO}_3^-$  oxidises  $\text{I}^-$  to  $\text{I}_2$  :



- $\text{ClO}_3^-$  oxidises  $\text{SO}_3^{2-}$  to  $\text{SO}_4^{2-}$  :



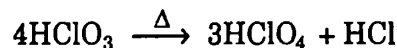
Following disproportionation of  $\text{ClO}_3^-$  also takes place as side reaction at low temperature and in the absence of catalyst :



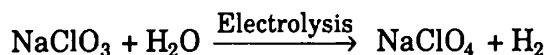
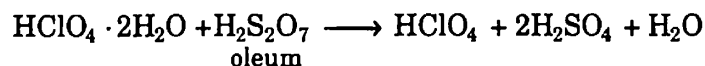
- Chlorates are used to make fireworks and matches.

### $\text{HXO}_4$ series

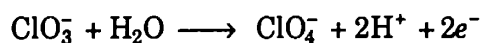
- $\text{HClO}_4$  and  $\text{HIO}_4$  and their salts are known.



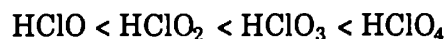
$\text{HClO}_4$  is commercially available as 70%  $\text{HClO}_4$  and is dihydrate  $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$  which can be dehydrated to  $\text{HClO}_4$  by oleum :



Oxidation of  $\text{ClO}_3^-$  occurs at a Pt anode through the half-reaction :



- $\text{HClO}_4$  is the strongest of all other oxoacids of Cl :



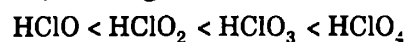
### DEEP Focus

- The dissociation of an oxoacid involves two energy terms : breaking an O—H bond to produce an anion and  $\text{H}^+$  ion

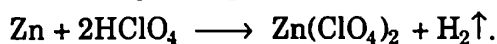


- hydrating both ions.

-  $\text{ClO}_4^-$  ion is larger than  $\text{OCl}^-$  so the hydration energy of  $\text{OCl}^-$  is larger than  $\text{ClO}_4^-$ . Also electronegativity of oxygen is greater than that of chlorine. In  $\text{HOCl}$ ,  $\text{HClO}_2$ ,  $\text{HClO}_3$ ,  $\text{HClO}_4$ , an increasing number of oxygen atoms are bonded to the chlorine atom. **The more oxygen atoms that are bonded, the more the electrons will be pulled away from the O—H bond, and the more this bond is weakened. Thus, greater the number of oxygen bonds attached to halogen, least is the energy required to break O—H bond, hence greater the acid strength**



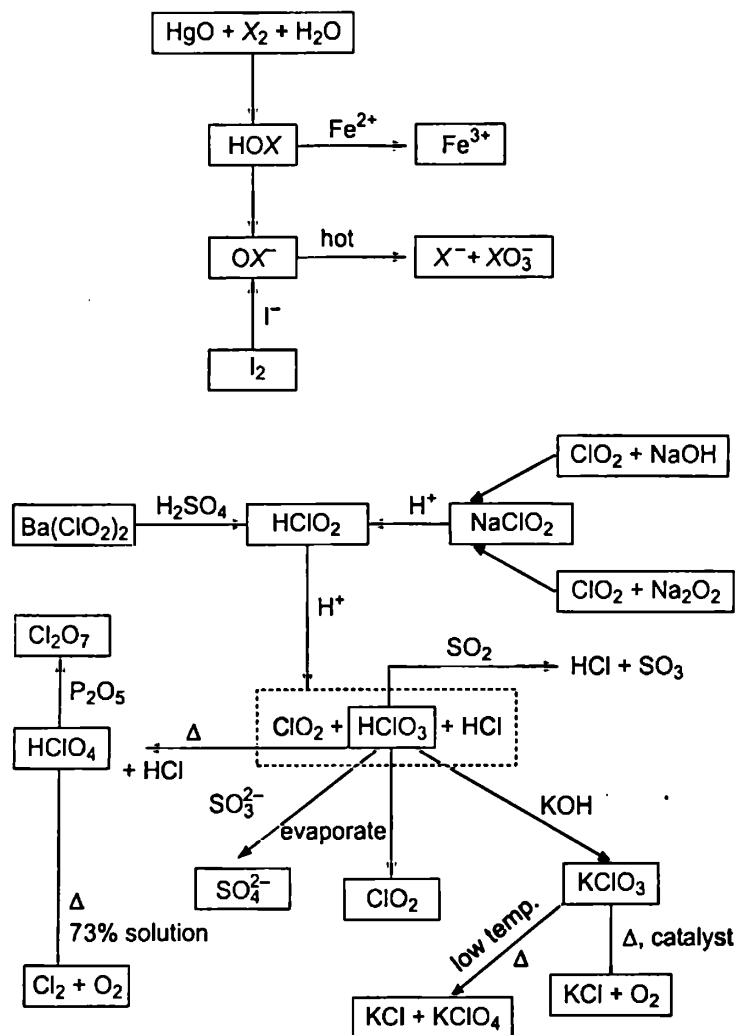
- Metals like Zn, Mg and Fe dissolve in dilute solutions of the acid forming their perchlorates:



Hot concentrated acid (73%) behaves as a remarkable oxidising agent:

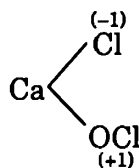


- $\text{Mg}(\text{ClO}_4)_2$  is used in **dry batteries** and is also a effective desiccant called **anhydron**.  $\text{KClO}_4$  is used in **fireworks and flares**.

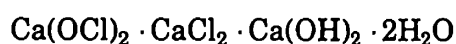
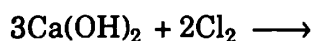


## Bleaching Powder

- Commonly it is written as  $\text{CaOCl}_2$  with one  $\text{Cl}^-$  and one  $\text{OCl}^-$  (hypochlorite) ions (**Cl with two different oxidation number**) and is thus calcium chloro hypochlorite



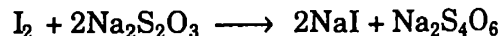
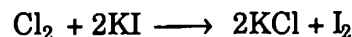
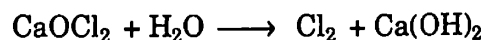
- Its actual composition is  $\text{Ca}(\text{OCl})_2 \cdot \text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  containing 35% available chlorine. It is obtained by action of  $\text{Cl}_2$  gas on slaked lime :



## DEEP Focus

"Available chlorine" content is defined as the weight of  $\text{Cl}_2$  which liberates the same amount of  $\text{I}_2$  from  $\text{HI}$  as does the given weight of the compound; it is expressed as a percentage.

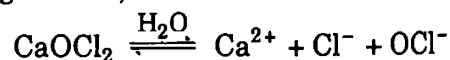
Available chlorine can be determined by treating aqueous solution of bleaching powder with  $\text{KI}$  and titrating liberated  $\text{I}_2$  using  $\text{Na}_2\text{S}_2\text{O}_3$  solution (hypo).  $\text{CH}_3\text{COOH}$  is also added to neutralise  $\text{Ca}(\text{OH})_2$  formed.



Thus,  $\text{CaOCl}_2 \equiv \text{Cl}_2 \equiv \text{I}_2 \equiv 2\text{Na}_2\text{S}_2\text{O}_3$

$$\text{Eq. wt. of CaOCl}_2 = \left( \frac{\text{molecular weight}}{2} \right)$$

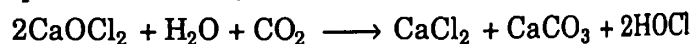
- Pale yellow solid with odour of  $\text{Cl}_2$ ; in aqueous solution it gives  $\text{Cl}^-$ ,  $\text{OCl}^-$  and  $\text{Ca}^{2+}$  ions :



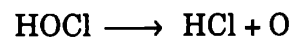
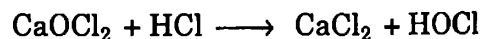
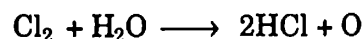
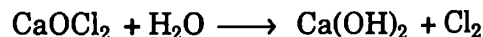
- It undergoes disproportionation on standing:



- When  $\text{CO}_2$  is passed into suspension of bleaching powder in water,  $\text{HOCl}$  is formed

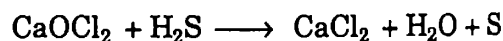


- It is a **bleaching agent** as well as **oxidising agent** due to oxygen formed in acidic medium/neutral medium :

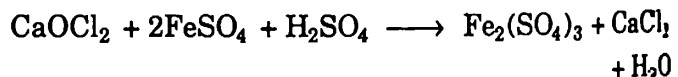


- $\text{CaOCl}_2$  oxidises

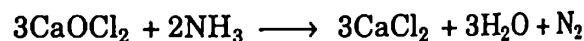
–  $\text{H}_2\text{S}$  into **S**



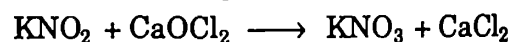
–  $\text{FeSO}_4$  into  **$\text{Fe}_2(\text{SO}_4)_3$**



–  $\text{NH}_3$  into  **$\text{N}_2$**

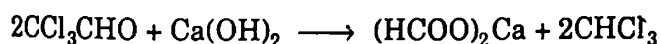
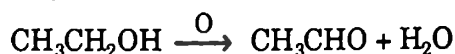
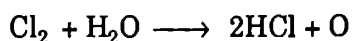
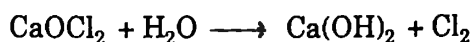


–  **$\text{KNO}_2$  into  $\text{KNO}_3$  and  $\text{Na}_3\text{AsO}_3$  into  $\text{Na}_3\text{AsO}_4$**



– **Carbonyl compounds** ( $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ ,  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ ) and **alcohols** ( $-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$ ) are oxidised to

**chloroform.**



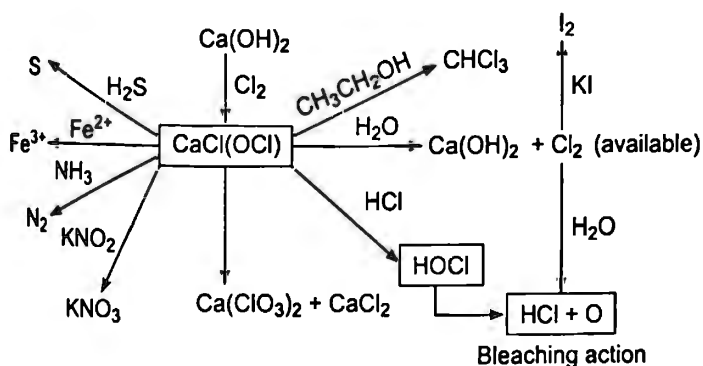
Similarly for  $\text{CH}_3\text{CHO}$ ,  $\text{RCOCH}_3$ . This test, called 'Halform test', is given by

-  $\text{CH}_3\text{CHO}$

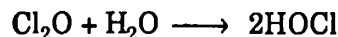
-  $\text{CH}_3\text{CH}_2\text{OH}$

- all 2° alcohols (at  $\text{C}_2$ )  $\begin{array}{c} \text{—CH—CH}_3 \\ | \\ \text{OH} \end{array}$

- all ketones (with carbonyl group at  $\text{C}_2$  as  $\begin{array}{c} \text{CH}_3\text{—C—} \\ || \\ \text{O} \end{array}$ )



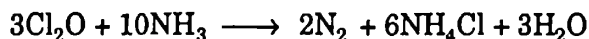
- It is soluble in water giving orange yellow coloured solution of  $\text{HOCl}$



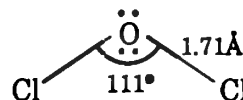
- It forms salt with alkali solution indicating its acidic character.



- It is an oxidising agent



- Structure is angular with  $sp^3$  hybridised O-atom and is related to a tetrahedron with two positions occupied by lone pairs of electrons.

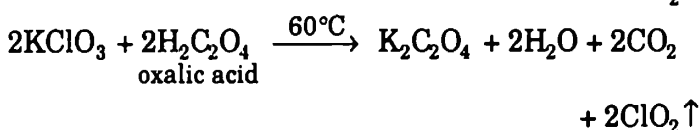


### DEEP Focus

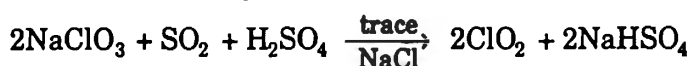
- The bond angle varies in the order  $\text{FOF} < \text{ClOCl} < \text{BrOBr}$ . This is because electrons in the case of  $\text{OF}_2$  are nearer to fluorine due to high electronegativity of F compared to Cl to Br. The bonded electron pairs in  $\text{Cl}_2\text{O}$  and  $\text{Br}_2\text{O}$  are closer to oxygen making the repulsion between them more and thereby reducing the lone pair-lone pair repulsion on oxygen to some extent. Also due to the bulkiness of Cl and Br, the angles  $\text{ClOCl}$  and  $\text{BrOBr}$  increase to such an extent that  $109^\circ 28'$ , (the tetrahedral angle), is approached.

### $\text{ClO}_2$ (Chlorine dioxide)

- $\text{ClO}_2$  (as yellow-coloured gas with unpleasant smell) is obtained when  $\text{KClO}_3$  reacts with conc.  $\text{H}_2\text{SO}_4$  or oxalic acid



- $2\text{AgClO}_3 + \text{Cl}_2 \xrightarrow{90^\circ\text{C}} 2\text{AgCl} \downarrow + 2\text{ClO}_2 \uparrow + \text{O}_2 \uparrow$
- Commercially it is prepared by passing  $\text{SO}_2$  gas into a mixture of  $\text{NaClO}_3$  and  $\text{H}_2\text{SO}_4$  having  $\text{NaCl}$  in traces.



- Aqueous solution of gas is neutral and is a strong oxidising agent :



### DEEP Focus

- $\text{ClO}_2$  reacts with  $\text{KOH}$  forming  $\text{KClO}_3$  and  $\text{KClO}_2$ .



This reaction indicates that  $\text{ClO}_2$  is a mixed anhydride of  $\text{HClO}_2$  and  $\text{HClO}_3$ .

## Oxides of Halogen

Following oxides of chlorine are known.

| Formula            | Name                    | Oxyacid         | Oxidation state of chlorine |
|--------------------|-------------------------|-----------------|-----------------------------|
| Chlorine monoxide  | $\text{Cl}_2\text{O}$   | $\text{HOCl}$   | +1                          |
| Chlorine dioxide   | $\text{ClO}_2$          | $\text{HClO}_2$ | +3                          |
| Chlorine hexoxide  | $\text{Cl}_2\text{O}_6$ | $\text{HClO}_3$ | +5                          |
| Chlorine heptoxide | $\text{Cl}_2\text{O}_7$ | $\text{HClO}_4$ | +7                          |

### $\text{Cl}_2\text{O}$ (Chlorine monoxide)

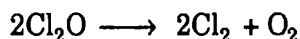
- When  $\text{Cl}_2$  gas is passed over  $\text{HgO}$  at  $300\text{--}500^\circ\text{C}$ ,  $\text{Cl}_2\text{O}$  is formed.



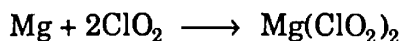
Reaction may also be carried out with chlorine dissolved in  $\text{CCl}_4$ .

- $\text{Cl}_2\text{O}$  is a brownish-yellow gas which condenses to an orange liquid (b.p.  $2^\circ\text{C}$ )

- It is thermally unstable and explodes on heating

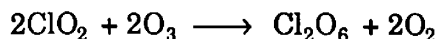


- It is strong oxidising agent and chlorinating agent :

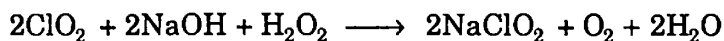


These metals in powdered form in aqueous suspension are oxidised.

- Ozone oxidises  $\text{ClO}_2$  to  $\text{Cl}_2\text{O}_6$



- Alkaline  $\text{H}_2\text{O}_2$  is oxidised to  $\text{O}_2$



- Cl atom is  $sp^3$  hybridised in the angular molecule with bond angle of  $118^\circ$  and Cl—O bond length of  $1.47\text{\AA}$ . It has odd number of electrons and is **thus paramagnetic** and the stability is due to the presence of 3-electron bonds stabilised by resonance. Molecules containing odd number of electrons are reactive and generally dimerise in order to pair the electrons, but  $\text{ClO}_2$  is the exception.



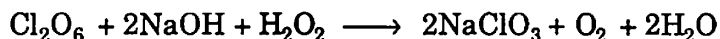
### $\text{Cl}_2\text{O}_6$ or $\text{ClO}_3$ [Chlorine hexoxide (trioxide)]

- When  $\text{ClO}_2$  reacts with ozonised  $\text{O}_2$  at  $0^\circ\text{C}$ ,  $\text{Cl}_2\text{O}_6$  is obtained.

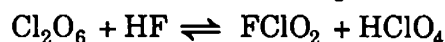


- $\text{Cl}_2\text{O}_6$  is unstable red oil (m.p.  $3.5^\circ\text{C}$ ) and explodes on heating.

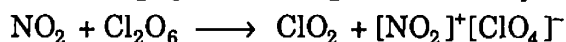
- It is a strong oxidising agent



- Anhydrous HF reversibly gives  $\text{FClO}_2$  and  $\text{HClO}_4$

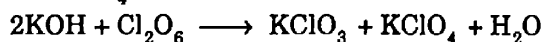


- $\text{NO} + \text{Cl}_2\text{O}_6 \longrightarrow \text{ClO}_2 + [\text{NO}]^+[\text{ClO}_4]^-$

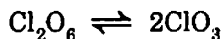


### DEEP Focus

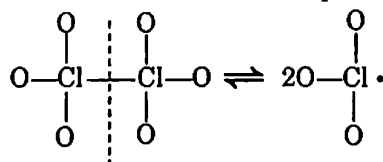
- When  $\text{Cl}_2\text{O}_6$  (or  $\text{ClO}_3$ ) reacts with  $\text{KOH}$ ,  $\text{KClO}_3$  and  $\text{KClO}_4$  are formed indicating that  $\text{Cl}_2\text{O}_6$  is a mixed anhydride of  $\text{HClO}_3$  and  $\text{HClO}_4$



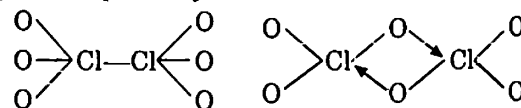
- In the liquid state and in aqueous solution, there is paramagnetism indicating existence of  $\text{ClO}_3$  formed due to dissociation of  $\text{Cl}_2\text{O}_6$



Paramagnetism is due to unpaired electrons in  $\text{ClO}_3$ ,  $\text{Cl}_2\text{O}_6$  is diamagnetic in solid state which is due to paired electrons.

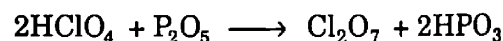


Solid has the ionic composition  $\text{ClO}_2^+ \text{ClO}_4^-$  confirmed by X-ray study. The liquid may have either of two structures :



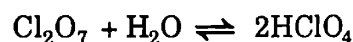
### $\text{Cl}_2\text{O}_7$ (Chlorine heptoxide)

- When  $\text{HClO}_4$  is added to  $\text{P}_2\text{O}_5$  at  $-10^\circ\text{C}$ ,  $\text{Cl}_2\text{O}_7$  is obtained which separates on distilling the mixture at  $85^\circ\text{C}$ .

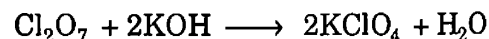


- $\text{Cl}_2\text{O}_7$  is colourless, oily liquid (b.p.  $82^\circ\text{C}$ )

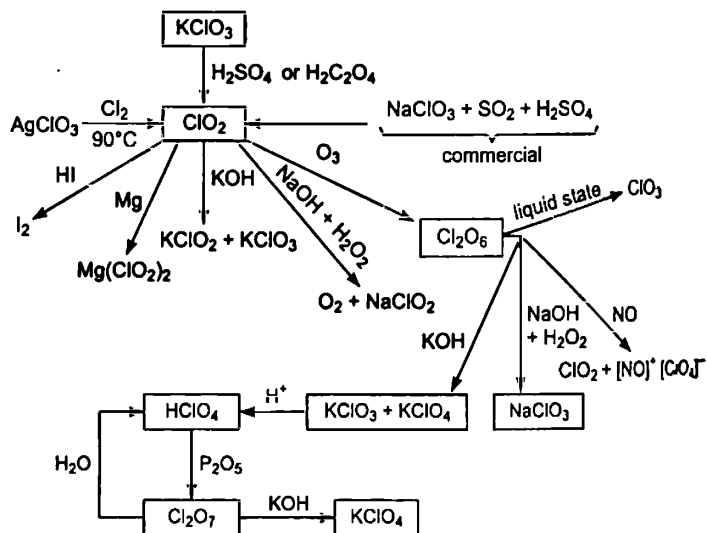
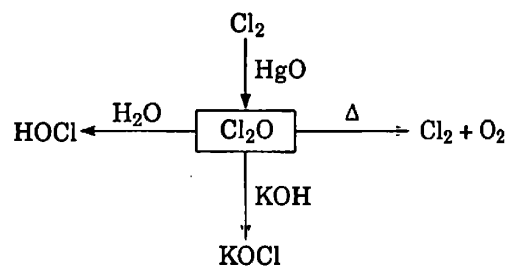
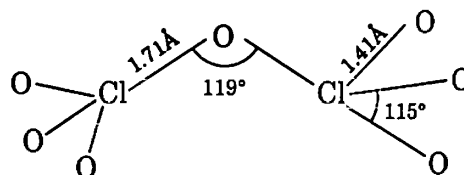
- $\text{Cl}_2\text{O}_7$  is extremely explosive.



- $\text{Cl}_2\text{O}_7$  reacts with alkali forming perchlorates.



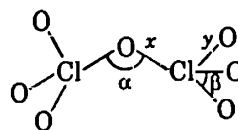
- $\text{Cl}_2\text{O}_7$  has a bent structure with a bridging O-atom. The terminal Cl—O bonds are substantially shorter than the bridge Cl—O bonds, indicating double bond character.



## Target Practice 2

- Arrange  $\text{HOCl}$ ,  $\text{HClO}_2$ ,  $\text{HClO}_3$  and  $\text{HClO}_4$  in increasing
  - oxidation state of halogen atom .....
  - oxidising power .....
  - acid strength .....
  - thermal stability .....
  - $s$ -character in hybridised state .....
- What are the anhydrides of
  - $\text{HOCl}$  .....
  - $\text{HClO}_2$  .....
  - $\text{HClO}_3$  .....
  - $\text{HClO}_4$  .....
- Mixture of  $\text{KBr}$  and  $\text{KBrO}_3$  in acidic medium can be used as brominating agent. Explain by chemical reaction  
.....  
.....
- $\text{KClO}_3$  is used .....
- $\text{KClO}_4$  is used as .....
- $\text{Mg}(\text{ClO}_4)_2$  is used as .....
- In aqueous solution bleaching powder reacts as  
 $\text{CaOCl}_2 + \text{H}_2\text{O} \longrightarrow \text{Cl}_2 + \text{Ca}(\text{OH})_2$

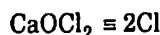
- $\text{Cl}_2$  thus, obtained is called .....
  - Equivalent weight of  $\text{CaOCl}_2$  is .....
  - What is the type of above reaction? .....
- Which of the following pairs can be distinguished by iodoform test?
    - $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{COCH}_3$
    - $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{CH}_2\text{OH}$
    - $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{CH}_2\text{OH}$
    - $\text{HCHO}$  and  $\text{CH}_3\text{CHO}$
  - Calculate magnetic moment of  $\text{Cl}_2\text{O}_8$  and  $\text{ClO}_3$ .
    - $\text{Cl}_2\text{O}_8$  ..... BM
    - $\text{ClO}_3$  ..... BM
  - Consider bond lengths  $x$  and  $y$  and bond angles  $\alpha$  and  $\beta$  in the following and compare these values



Bond lengths :  $x$  ☐  $y$   
Bond angles :  $\alpha$  ☐  $\beta$

## Answers

- $\text{HOCl} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$
  - $\text{HOCl} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$
  - $\text{HOCl} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$
  - $\text{HOCl} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$
  - Equal (25%) each Cl-atom is  $sp^3$  hybridised.
- (a)  $\text{Cl}_2\text{O}$  (b)  $\text{ClO}_2$  (c)  $\text{Cl}_2\text{O}_6$  (d)  $\text{Cl}_2\text{O}_7$
- $5\text{Br}^- + \text{BrO}_3^- + 6\text{H}^+ \longrightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$
- (a) an explosive, (b) fireworks and flares  
(c) dry batteries
- available chlorine  
(b)  $\text{CaOCl}_2 \equiv 2\text{Cl}_2 \equiv 2\text{Cl}$



$$\therefore \text{Equivalent weight} = \frac{\text{Molecular weight}}{2}$$

- There are two types of Cl in  $\text{CaOCl}_2$   
 $\text{Cl}^-$  (oxidation number = -1) oxidised to  $\text{Cl}_2$   
 $\text{ClO}^-$  (oxidation number = +1) reduced to  $\text{Cl}_2$   
Thus, it is an intramolecular redox reaction
- (a) No (b) No (c) Yes (d) Yes
- (a) Zero BM (no unpaired electron)  
(b)  $\sqrt{3}$  BM (with one unpaired electron)
- (a)  $x > y$  (b)  $\alpha > \beta$

## Practice Exercise 2

- Complete following reactions :
  - $\text{ClO}_3^- + \text{I}^- + 6\text{H}^+ \longrightarrow$
  - $\text{ClO}_3^- + \text{Fe}^{2+} + \text{H}^+ \longrightarrow$
  - $\text{Zn}(\text{ClO}_3)_2 \xrightarrow{\Delta}$
  - $\text{O}_3 + \text{I}_2 + \text{H}_2\text{O} \longrightarrow$
  - $\text{KBrO}_3 + \text{F}_2 + \text{KOH} \longrightarrow$
- Which is stronger acid in each pair ?
  - $\text{HClO}$      $\text{HClO}_2$     (b)  $\text{H}_2\text{SO}_4$      $\text{H}_2\text{SO}_3$
  - $\text{H}_3\text{PO}_2$      $\text{H}_3\text{PO}_3$     (d)  $\text{HNO}_3$      $\text{HNO}_2$
  - $\text{HF}$      $\text{HCl}$     (f)  $\text{H}_3\text{PO}_3$      $\text{H}_3\text{PO}_4$
- $\text{C}_6\text{H}_5\text{O}$  gives iodoform test. Identify it.
- $\text{C}_6\text{H}_5\text{O}$  (A)  $\xrightarrow[\Delta]{\text{CaOCl}_2/\text{H}_2\text{O}}$   $\text{CHCl}_3 + \text{(B)}$   
(B)  $\xrightarrow{\text{H}^+}$ 

What are (A) and (B)?

- 10 g of bleaching powder is dissolved in water containing some  $\text{CH}_3\text{COOH}$  and diluted to 1 L. 20 mL of this solution on reaction with KI required 20 mL of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Calculate percentage of available chlorine in it.
- $\text{CaOCl}_2$  in aqueous solution changes to  $\text{Cl}_2$ . What is the type of this change ?
- Give structure of oxoacids of halogens.
- What are the corresponding anhydrides of the following oxyacids,  
 $\text{HClO}_4$ ,  $\text{HClO}_3$ ,  $\text{HClO}_2$  and  $\text{HOCl}$
- Identify A, B and C in the following  

$$\begin{array}{ccc} \text{HClO}_4 + \text{P}_2\text{O}_5 & \longrightarrow & \text{A} + \text{B} \\ & & \downarrow \text{KOH} \\ & & \text{C} + \text{H}_2\text{O} \end{array}$$



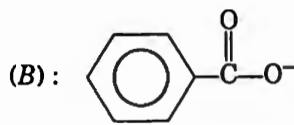
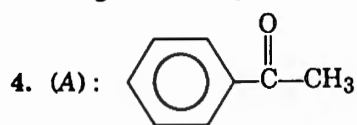
## Answers

1. (a)  $\text{ClO}_3^- + 6\text{I}^- + 6\text{H}^+ \longrightarrow \text{Cl}^- + 3\text{I}_2 + 3\text{H}_2\text{O}$   
 (b)  $\text{ClO}_3^- + 6\text{Fe}^{2+} + 6\text{H}^+ \longrightarrow \text{Cl}^- + 6\text{Fe}^{3+} + 3\text{H}_2\text{O}$   
 (c)  $2\text{Zn}(\text{ClO}_3)_2 \xrightarrow{\Delta} 2\text{ZnO} + 2\text{Cl}_2 + 5\text{O}_2$   
 (d)  $3\text{O}_3 + \text{I}_2 + \text{H}_2\text{O} \longrightarrow 2\text{IO}_3^- + 2\text{O}_2 + 2\text{H}^+$   
 (e)  $\text{KBrO}_3 + \text{F}_2 + 2\text{KOH} \longrightarrow \text{KBrO}_4 + 2\text{KF} + \text{H}_2\text{O}$

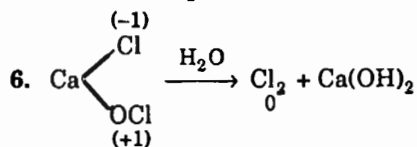
2. (a)  $\text{HClO}_2$  (b)  $\text{H}_2\text{SO}_4$  (c) almost same (d)  $\text{HNO}_3$   
 (e)  $\text{HCl}$  (f) almost same

In  $\text{H}_3\text{PO}_2$ ,  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_4$ , terminal O is one, and electronegativity values of P and H are almost same, hence, acid strengths of these acids are same.

3.  $\text{CH}_3-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CH}_2-\text{CH}_3$  (it should have  $\text{CH}_3-\overset{\text{O}}{\text{C}}-$  group of the given carbonyl formula)



5.  $\text{CaOCl}_2 \equiv \text{Cl}_2 \equiv \text{I}_2 \equiv 2\text{Na}_2\text{S}_2\text{O}_3$   
 $\text{CaOCl}_2 \equiv \text{Cl}_2 \equiv \text{I}_2 \equiv 0.1\text{N} (N_1 V_1 = N_2 V_2)$   
 $\text{Cl}_2 = 3.55 \text{ g L}^{-1}$  in  $10 \text{ g L}^{-1}$  bleaching powder.  
 Available  $\text{Cl}_2 = 35.5\%$



$\text{Cl}^-$  (alone) is oxidised to  $\text{Cl}_2$  and  $\text{Cl}$  (of  $\text{OCl}$ ) is reduced to  $\text{Cl}_2$ . Hence, it is a redox reaction.

7. (a)  $\text{H}-\text{O}-\ddot{\text{Cl}}:$  (b)  $\text{H}-\text{O}-\ddot{\text{Cl}}: \longrightarrow \text{O}$   
 (c)  $\text{H}-\text{O}-\ddot{\text{Cl}}: \longrightarrow \text{O}$  (d)  $\text{H}-\text{O}-\ddot{\text{Cl}}: \longrightarrow \text{O}$

In all cases Cl atom is  $sp^3$  hybridised.

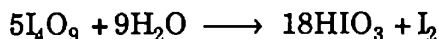
8.  $\text{HClO}_4 : \text{Cl}_2\text{O}_7$ ;  $\text{HClO}_3 : \text{Cl}_2\text{O}_6$ ;  $\text{HClO}_2 : \text{ClO}_2$ ;  
 $\text{HOCl} : \text{Cl}_2\text{O}$   
 9. (A) :  $\text{Cl}_2\text{O}_7$  (B) :  $\text{HPO}_3$  (C) :  $\text{KClO}_4$ .

Hence, from the concentration of  $\text{HCl}$ ,  $\text{HOCl}$  and  $\text{Cl}_2$  equilibrium constant can be determined.

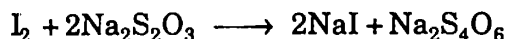
To determine  $\Delta H$  (standard enthalpy change) we measure value of equilibrium constant  $K$  at different temperature and using van't Hoff equation,

$$\Delta H = \frac{2.303RT_1T_2}{(T_2 - T_1)} \log \frac{K_2}{K_1}$$

**Problem 5.** Describe in outline how you would attempt to show that oxide  $I_4O_9$ , reported to be formed by the action of ozone on iodine, reacts with water according to the equation,



**Solution** Neutralise the solution of a weighted amount of the oxide with  $NaHCO_3$  and titrate the  $I_2$  against  $Na_2S_2O_3$  (sodium thiosulphate) solution,



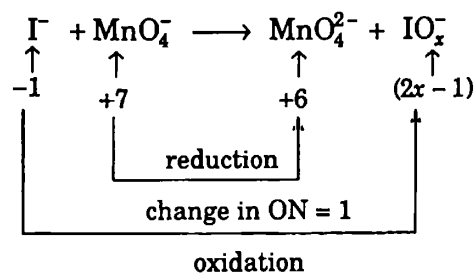
There is consumption of  $Na_2S_2O_3$  due to formation of  $I_2$ , hence,  $I_4O_9$  reacts with  $H_2O$  to give  $I_2$ .

**Problem 6.** In a strongly alkaline solution containing excess of barium ions, a solution containing 0.01587 g of  $I^-$  was treated with 0.1 M  $MnO_4^-$  until a pink colour persisted in the solution. 10.0 mL of the  $MnO_4^-$  solution were required. Under these conditions  $MnO_4^-$  is converted into the sparingly soluble  $BaMnO_4$ . What is the product of oxidation of the iodide? ( $I = 127$ )

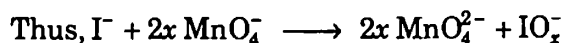
**Solution** Let oxidation product of  $I^-$  by  $MnO_4^- = IO_x^-$

Oxidation number of I in  $IO_x^- = n = (2x - 1)$

$MnO_4^-$  is reduced to  $MnO_4^{2-}$  in the oxidation of  $I^-$ . Thus,



change in ON =  $2x$

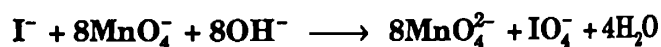


$$1 \text{ mol } I^- = 2x \text{ mol of } MnO_4^-$$

$$\begin{aligned} \frac{0.01587}{127} \text{ mol } I^- &= \frac{2x \times 0.01587}{127} \text{ mol } MnO_4^- \\ &= \frac{10 \times 0.1}{1000} \end{aligned}$$

$$x = 4$$

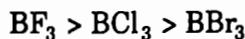
Thus, oxidation product of  $I^-$  is  $IO_4^-$  and



## Explanation

(a) The polarity of B—X bonds is in the order : B—F > B—Cl > B—Br but Lewis acidity shows the sequence :  $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$ .

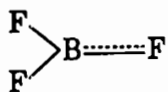
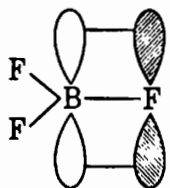
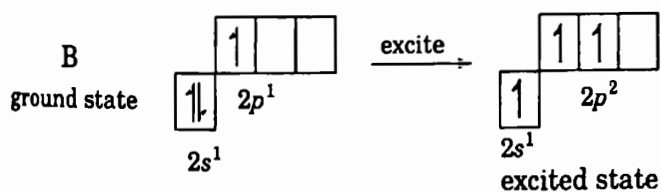
— With increase in polarity of B—X bond, acidity also increases and should be thus in the order :



But Lewis acidity is in reverse order :



There is lateral overlap of the vacant  $2p$  orbital of B with one completely filled orbital of F leading to  $p\pi-p\pi$  bonds between B and F. This B—F bond thus acquires double bond character. This also leads to compensate electron deficiency of boron and thus Lewis acid character of  $\text{BF}_3$  is reduced. This  $p\pi-p\pi$  bonding decreases going from  $\text{BF}_3$  to  $\text{BBr}_3$  and thus Lewis acidic nature increases in the order :

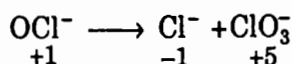


(b)  $\text{NF}_3$  is stable while  $\text{NCl}_3$  and  $\text{NI}_3$  are explosive.

— In  $\text{NF}_3$  the electronegativity difference ( $\text{N} = 3.0$ ;  $\text{F} = 4.0$ ) permits strong  $p_\pi - p_\pi$  bonding and the molecule is stable. But in  $\text{NCl}_3$  and  $\text{NI}_3$ , the electronegativity difference is nil or small and the molecules are unstable with  $p_\pi - p_\pi$  bonding weak. Hence,  $\text{NF}_3$  is a stable gas,  $\text{NCl}_3$  an explosive liquid and  $\text{NI}_3$  an explosive solid.

(c) In the series  $\text{HXO}$ , the order of stability is :  $\text{HOCl} > \text{HOBr} > \text{HOI}$

—  $\text{HOX}$  and  $\text{OX}^-$  are unstable and undergo disproportionation :

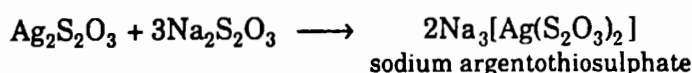
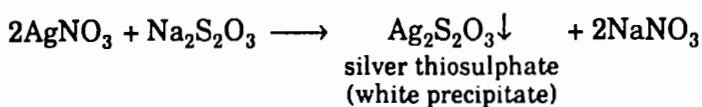


The instability is due to decrease in bond energy from chlorine to iodine.

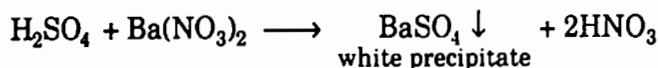
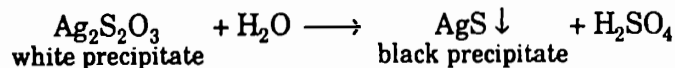
(d) Silver nitrate gives a white precipitate with aqueous sodium thiosulphate; the precipitate

dissolves in excess of thiosulphate. If the precipitate is heated with water it turns black, and the supernatant liquid then gives a white precipitate with acidified barium nitrate solution.

— When sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) solution is added to silver nitrate ( $\text{AgNO}_3$ ) solution, there is a white precipitate due to the formation silver thiosulphate ( $\text{Ag}_2\text{S}_2\text{O}_3$ ); these precipitate dissolve in excess of sodium thiosulphate due to the formation of the complex  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ .



If the precipitate of  $\text{Ag}_2\text{S}_2\text{O}_3$  is heated, there is disproportionation giving black precipitate of  $\text{Ag}_2\text{S}$  and soluble  $\text{H}_2\text{SO}_4$  which remains in the upper (supernatant) layer which gives white precipitate (of  $\text{BaSO}_4$ ) with  $\text{Ba}(\text{NO}_3)_2$  solution.



(e) Silver chloride and silver iodide are soluble in saturated aqueous potassium iodide, but insoluble in saturated aqueous potassium chloride.

— Iodide complex of silver must be more stable than chloride complex.

(f) Although the hydrogen bonding in hydrogen fluoride is stronger than that in water, water has much the higher boiling-point.

— Hydrogen fluoride vapour is polymeric, hence, the hydrogen bonds are not broken on volatisation; those in water are broken thus requiring higher enthalpy. Hence, boiling point of  $\text{H}_2\text{O}$  is higher than that of  $\text{HF}$ .

(g) Fluorine combines with other elements in the higher oxidation states.

— Following factors contribute the unique ability of fluorine to combine with other elements in their higher oxidation states.

- (i) the highest oxidising power
- (ii) high lattice energy of fluoride
- (iii) high enthalpy of hydration of fluoride
- (iv) lower F—F bond energy of F—F bond

(h) *The bond dissociation energy increases from  $I_2$  to  $Cl_2$ . Thus, bond dissociation energy of  $F_2$  should be higher than that of  $Cl_2$ . But it is not so.*

- Fluorine has the smallest size of all the halogens. There is considerable repulsion in the non-bonding electrons which weakens the F—F bond. Thus, bond dissociation energy of  $F_2$  is less than that of  $Cl_2$ .

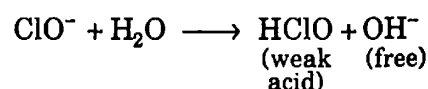
(i) *HF is the weakest acid*

- HF has the highest bond dissociation enthalpy amongst all the halogen acids. The hydration enthalpy of the fluoride ion is also highest, the former predominates making HF the weakest of the halogen acids.

(j) *Salts of hypohalous acids are alkaline in nature due to hydrolysis.*

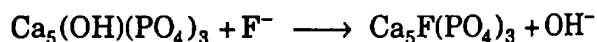
- NaClO (sodium hypochlorite) is a salt of HClO (hypochlorous acid) and NaOH. HClO is a fairly weak

acid. On hydrolysis  $ClO^-$  forms HClO (weak acid) and free  $OH^-$  ions which makes the solution alkaline.



(k) *Tap water requires fluoridation.*

- The main constituent of tooth enamel is  $Ca_5(OH)(PO_4)_3$  called hydroxyapatite, which in presence of fluoride ions is converted into harder, acid-resistant fluorapatite,  $Ca_5F(PO_4)_3$



Thus, addition of fluoride makes the teeth harder and prevents their decay. If we use tap water deficient in fluoride, it can cause formation of cavity.

**Imp** Paradoxically, consuming 2 ppm or more fluoride also causes mottling of teeth.

# Master Exercises

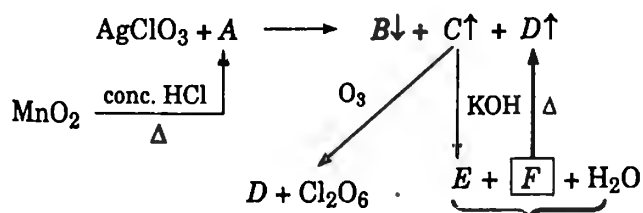
## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

- Sea water contains around  $65 \times 10^{-3}$  g of bromide ions in  $1 \text{ dm}^3$ . If all the bromide ions are converted into  $\text{Br}_2$ , how many  $\text{dm}^3$  of sea-water are needed to produce 1 kg of bromine  $\text{Br}_2$ ?
- Complete the following reactions:
  - $\text{CH}_3\text{CH}=\text{CH}_2 + \text{ICl} \longrightarrow$
  - $\text{Cl}_2 + \text{NaOH} \xrightarrow{\text{hot}} \longrightarrow$
  - $\text{Cl}_2 + \text{S}^{2-} \longrightarrow$
  - $\text{SO}_2 + \text{I}_2 + \text{H}_2\text{O} \longrightarrow$
  - $\text{SnCl}_2 + \text{HCl} + \text{I}_2 \longrightarrow$
- $\text{I}_3^-$  is formed when  $\text{I}_2$  combines with  $\text{I}^-$ . Which of them is a Lewis base?
- Which is **stronger base** in each pair?
 

|                      |                  |                                |                           |
|----------------------|------------------|--------------------------------|---------------------------|
| (a) $\text{ClO}_2^-$ | $\text{ClO}_3^-$ | (b) $\text{OH}^-$              | $\text{CN}^-$             |
| (c) $\text{I}^-$     | $\text{Cl}^-$    | (d) $\text{CH}_3\text{CH}_2^-$ | $\text{CH}_2=\text{CH}^-$ |
| (e) $\text{NO}_3^-$  | $\text{NO}_2^-$  | (f) $\text{H}_2\text{PO}_2^-$  | $\text{H}_2\text{PO}_3^-$ |

- Iodine pentoxide,  $\text{I}_2\text{O}_5$ , is sometimes used to remove CO from the air by forming  $\text{CO}_2$  and  $\text{I}_2$ . Write a balanced equation for this reaction and identify species that are oxidised and reduced.
- $\text{HOCl}$  can also be prepared by passing  $\text{CO}_2$  through a suspension of bleaching powder in water. Write balanced equation for this reaction.
- $\text{Cl}_2\text{O}_6$  is diamagnetic but in liquid state, it shows paramagnetism. Explain.
- Identify A to F in the following :



- Name the halogen

- has two complete electron shells below the valence shells
- is solid at room temperature
- has highest electronegativity value
- lowest ionisation energy
- lowest formation of  $\text{X(g)}$

- Complete the following reactions

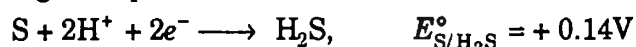
- $\text{I}_2 + \text{IF}_3 \longrightarrow$
- $\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow$
- $\text{Cl}_2 + \text{H}_2\text{S} \longrightarrow$

- Write the names of the following oxoacids and deduce the oxidation number of halogen atom in each

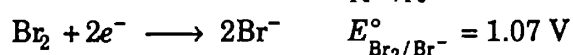
- |                     |                      |
|---------------------|----------------------|
| (a) $\text{HOCl}$   | (b) $\text{HOClO}$   |
| (c) $\text{HOBr}$   | (d) $\text{HOBrO}_2$ |
| (e) $\text{HOIO}_3$ | (f) $\text{HOClO}_3$ |

### Analytical Questions

- The redox reaction involving the reducing power of hydrogen sulphide is :



Two other half equations are :



Under standard conditions :

- will hydrogen sulphide react with iron (III) ions?
- will it react with bromine?

If you decide a reaction should take place, write the equation.

- Explain :

- Electron affinity of Cl is the highest among the halogens; yet,  $\text{F}_2$  is the strongest oxidising agent.
- $\text{ClO}_2$  is a free radical with one unpaired electron but has no tendency to dimerise like  $\text{NO}_2$ .
- $\text{HCl(g)}$  and  $\text{HCl(aq)}$  have different behaviour towards litmus.

3. 0.01 M solutions of iodine in *n*-hexane, benzene, ethanol and pyridine are violet, purple, brown and yellow respectively. When 0.001 mol of pyridine is added to 100 mL of each of the solutions of iodine in

*n*-hexane, benzene and ethanol, all of these become yellow, Explain.

## Exercise 2

### (Stage 2 : High Skill Problem Solving)

#### Only One Option Correct

- Of the following acids  
I : Hypophosphorus acid  
II : Oxalic acid  
III : Glycine  
(a) I, II are monobasic; III dibasic and amphoteric  
(b) II monobasic; I, dibasic acid; III amphoteric  
(c) I monobasic, II, dibasic, III amphoteric  
(d) I, II dibasic; III amphoteric
- Which incorrect statement?  
(a) All halogens form oxyacids  
(b) All halogens show -1, +1, +3, +5, +7 oxidation states  
(c) Hydrofluoric acid forms  $\text{KHF}_2$  and  $\text{K}_2\text{F}_2$  and attacks glass  
(d) Oxidising power is in order  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- $\text{HClO}_4$ ,  $\text{HNO}_3$  and  $\text{HCl}$  are all very strong acids in aqueous solution. In glacial acetic acid medium, their acid strength is such that  
(a)  $\text{HClO}_4 > \text{HNO}_3 > \text{HCl}$   
(b)  $\text{HNO}_3 > \text{HClO}_4 > \text{HCl}$   
(c)  $\text{HCl} > \text{HClO}_4 > \text{HNO}_3$   
(d)  $\text{HCl} > \text{HClO}_4 \sim \text{HNO}_3$
- Tincture of iodine is  
(a)  $\text{CHI}_3$  in alcohol  
(b)  $\text{I}_2$  in alcohol  
(c)  $\text{I}_2$  in KI  
(d)  $\text{CHI}_3$  in KI
- "Chlorine-type" laundry bleaches are in reality aqueous solution of  
(a)  $\text{HOCl}$   
(b)  $\text{HClO}_3$   
(c)  $\text{NaClO}_3$   
(d)  $\text{NaOCl}$
- The active constituent of bleaching powder is  
(a)  $\text{Ca}(\text{OCl})_2$   
(b)  $\text{Ca}(\text{OCl})\text{Cl}$   
(c)  $\text{Ca}(\text{ClO}_2)_2$   
(d)  $\text{Ca}(\text{ClO}_2)\text{Cl}$
- Which one of the following is the weakest base as per the Bronsted concept?  
(a)  $[\text{ClO}_4]^-$   
(b)  $[\text{ClO}_3]^-$   
(c)  $[\text{ClO}_2]^-$   
(d)  $[\text{ClO}]^-$
- Which one of the following is not a true "per acid"?  
(a)  $\text{HClO}_4$   
(b)  $\text{H}_2\text{SO}_5$   
(c)  $\text{H}_2\text{S}_2\text{O}_8$   
(d)  $\text{H}_3\text{PO}_5$
- Which is/are true statement(s)?  
(a) Basic nature of  $X^-$  is in order  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$   
(b) HI is strongest acid of HF, HCl, HBr and HI  
(c) The ionic character of  $M-X$  bond decreases in the order  $M-F > M-Cl > M-Br > M-I$   
(d) All the above are correct statements
- Select incorrect statement.  
(a)  $\text{ClO}_2$  and  $\text{Cl}_2\text{O}$  are used as bleaching agents for paper pulp and textiles  
(b)  $\text{OCl}^-$  (hypochlorites) salts are used as detergent  
(c)  $\text{OCl}^-$  disproportionates in alkaline medium  
(d)  $\text{BrO}_3^-$  is oxidised to  $\text{Br}_2$  by  $\text{Br}^-$  in acidic medium
- Consider the following boron halides:  
I.  $\text{BF}_3$   
II.  $\text{BCl}_3$   
III.  $\text{BBr}_3$   
IV.  $\text{BI}_3$   
The Lewis acid characters of these halides are such that  
(a)  $\text{I} < \text{II} < \text{III} < \text{IV}$   
(b)  $\text{I} < \text{III} < \text{II} < \text{IV}$   
(c)  $\text{IV} < \text{III} < \text{II} < \text{I}$   
(d)  $\text{IV} < \text{II} < \text{III} < \text{I}$
- Which of the following compounds possesses Lewis acid character?  
I.  $\text{BF}_3$   
II.  $\text{SiF}_4$   
III.  $\text{PF}_5$   
Select the correct answer using the codes given below  
**Codes**  
(a) I alone  
(b) I, II and III  
(c) II and III  
(d) I and III
- Inter-halogen compounds can be  
(a)  $\text{ICl}_3$   
(b)  $\text{BrF}_5$   
(c)  $\text{IF}_7$   
(d) all of these
- Oxidation of hydrogen halide,  $\text{HX}$  affords a method for the industrial and laboratory preparation of the halogen,  $\text{X}_2$ , in the free state in respect of all of the following except  
(a) fluorine  
(b) chlorine  
(c) bromine  
(d) iodine
- Which of the following statements are correct for all three halogens (X), Cl, Br and I?  
(a) They all need to gain one electron to acquire stable configuration  
(b) They all form strong acid of the type  $\text{HX}$   
(c) Both (a) and (b) are correct  
(d) None of the above is correct

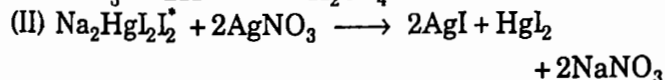
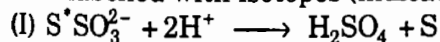
16. Which of the underlined atoms in oxyacids have  $sp^3$  hybridised atoms?  
 (a)  $\text{H}\underline{\text{C}}\text{ClO}_4$ ,  $\text{H}_2\underline{\text{S}}\text{O}_4$ ,  $\text{H}\underline{\text{N}}\text{O}_2$   
 (b)  $\text{H}_2\underline{\text{S}}\text{O}_4$ ,  $\text{H}_3\underline{\text{P}}\text{O}_4$ ,  $\text{H}\underline{\text{N}}\text{O}_3$   
 (c)  $\text{H}\underline{\text{C}}\text{ClO}_4$ ,  $\text{H}_2\underline{\text{S}}\text{O}_4$ ,  $\text{H}_2\underline{\text{S}}\text{O}_5$   
 (d)  $\text{H}\underline{\text{C}}\text{ClO}_4$ ,  $\text{H}\underline{\text{N}}\text{O}_3$ ,  $\text{H}\underline{\text{C}}\text{ClO}_3$
17. In the following  
 (a)  $\text{CsI}_3$  will ionise to give  $\text{Cs}^+$  and  $\text{I}_3^-$   
 (b)  $\text{RbICl}_2$  will give  $\text{RbCl}$  and  $\text{ICl}$   
 (c)  $\text{KBrICl}$  will give  $\text{KCl}$  and  $\text{IBr}$   
 (d) all of the above are correct
18. Which of the following atoms has the highest ionisation energy?  
 (a) F (b) Cl  
 (c) Br (d) I
19. Which one of the following arrangements does not truly represent the property indicated against it?  
 (a)  $\text{Br}_2 < \text{Cl}_2 < \text{F}_2$  : Oxidising power  
 (b)  $\text{Br} < \text{Cl} < \text{F}$  : Electronegativity  
 (c)  $\text{Br} < \text{F} < \text{Cl}$  : Electron affinity  
 (d)  $\text{Br}_2 < \text{Cl}_2 < \text{F}_2$  : Bond energy
20. The mixture of concentrated  $\text{HCl}$  and  $\text{HNO}_3$  made in 3:1 ratio contains  
 (a)  $\text{ClO}_2$  (b)  $\text{NOCl}$   
 (c)  $\text{NCl}_3$  (d)  $\text{N}_2\text{O}_4$
21. The formula for calcium chlorite is  
 (a)  $\text{Ca}(\text{ClO}_4)_2$  (b)  $\text{Ca}(\text{ClO}_3)_2$   
 (c)  $\text{CaClO}_2$  (d)  $\text{Ca}(\text{ClO}_2)_2$
22. Which one of the following oxoacids of chlorine is the least oxidising in nature?  
 (a)  $\text{HClO}$  (b)  $\text{HClO}_2$   
 (c)  $\text{HClO}_3$  (d)  $\text{HClO}_4$
23. Least stable oxide of chlorine is  
 (a)  $\text{Cl}_2\text{O}_4$  (b)  $\text{ClO}_2$   
 (c)  $\text{Cl}_2\text{O}_7$  (d)  $\text{Cl}_2\text{O}_6$
24. Which reaction is not feasible?  
 (a)  $2\text{KI} + \text{Br}_2 \longrightarrow 2\text{KBr} + \text{I}_2$   
 (b)  $2\text{KBr} + \text{I}_2 \longrightarrow 2\text{KI} + \text{Br}_2$   
 (c)  $2\text{KBr} + \text{Cl}_2 \longrightarrow 2\text{KCl} + \text{Br}_2$   
 (d)  $2\text{H}_2\text{O} + 2\text{F}_2 \longrightarrow 4\text{HF} + \text{O}_2$
25. Shape of  $\text{O}_2\text{F}_2$  is similar to that of  
 (a)  $\text{C}_2\text{F}_2$  (b)  $\text{H}_2\text{O}_2$   
 (c)  $\text{H}_2\text{F}_2$  (d)  $\text{C}_2\text{H}_2$
26. Iodine test is shown by  
 (a) glucose (b) starch  
 (c) glycogen (d) polypeptide
27. Which one will liberate  $\text{Br}_2$  from  $\text{KBr}$ ?  
 (a)  $\text{I}_2$  (b)  $\text{SO}_2$   
 (c)  $\text{HI}$  (d)  $\text{Cl}_2$
28. An important product in the ozone depletion by chlorofluorocarbons is  
 (a)  $\text{Cl}_2$  (b)  $\text{OCl}$   
 (c)  $\text{F}_2$  (d)  $\text{O}_2\text{F}_2$
29. Which one is the strongest bond?  
 (a)  $\text{Br}-\text{F}$  (b)  $\text{F}-\text{F}$   
 (c)  $\text{Cl}-\text{F}$  (d)  $\text{Br}-\text{Cl}$
30. The interhalogen compound not obtained is  
 (a)  $\text{ICl}$  (b)  $\text{IF}_5$   
 (c)  $\text{BrF}_5$  (d)  $\text{BrCl}_7$
31. Which of the following will displace the halogen from the solution of the halide?  
 (a)  $\text{Br}_2$  added to  $\text{NaI}$  (b)  $\text{Br}_2$  added to  $\text{NaCl}$   
 (c)  $\text{Cl}_2$  added to  $\text{KCl}$  (d)  $\text{Cl}_2$  added to  $\text{NaF}$
32. Which is the strongest oxidising agent out of the following?  
 (a)  $\text{I}_2$  (b)  $\text{Cl}_2$   
 (c)  $\text{Br}_2$  (d)  $\text{F}_2$
33. The high oxidising power of fluorine is due to  
 (a) high electron affinity  
 (b) high heat of dissociation and low heat of hydration  
 (c) low heat of dissociation and high heat of hydration  
 (d) high heat of dissociation and high heat of hydration
34. When  $\text{Cl}_2$  is passed through cold dil.  $\text{NaOH}$ , the products are  
 (a)  $\text{NaCl}$ ,  $\text{NaOCl}$  and  $\text{H}_2\text{O}$   
 (b)  $\text{NaCl}$ ,  $\text{NaClO}_2$  and  $\text{H}_2\text{O}$   
 (c)  $\text{NaCl}$ ,  $\text{NaClO}_3$  and  $\text{H}_2\text{O}$   
 (d)  $\text{NaCl}$ ,  $\text{NaClO}_4$  and  $\text{H}_2\text{O}$
35. The greater reactivity of  $\text{F}_2$  is due to  
 (a) lower electron affinity of F  
 (b) lower bond energy of  $\text{F}-\text{F}$  bond  
 (c) higher electronegativity of F  
 (d) gaseous state of  $\text{F}_2$
36. Dissociation of  $\text{HI}$  into  $\text{H}_2$  and  $\text{I}_2$  is  
 (a) kinetically controlled  
 (b) thermodynamically controlled  
 (c) kinetically as well as thermodynamically controlled  
 (d) neither kinetically nor thermodynamically controlled
37. In the preparation of  $\text{HBr}$  or  $\text{HI}$ ,  $\text{NaX}$  ( $X = \text{Br}, \text{I}$ ) is treated with  $\text{H}_3\text{PO}_4$  and not by conc.  $\text{H}_2\text{SO}_4$  and since  
 (a)  $\text{H}_2\text{SO}_4$  makes the reaction reversible  
 (b)  $\text{H}_2\text{SO}_4$  oxidises  $\text{HX}$  to  $\text{X}_2$  ( $\text{Br}, \text{I}$ )  
 (c)  $\text{Na}_3\text{PO}_4$  is water soluble  
 (d)  $\text{Na}_2\text{SO}_4$  is water soluble



38. Acid strength of  $HX$  ( $X = F, Cl, Br, I$ ) is dependent on  
 (a) the electronegativity differences of H and X  
 (b) the tendency of the hydrated molecule to form  $H^+$   
 (c) both (a) and (b)  
 (d) None of the above
39. Select correct statement(s) regarding behaviour of HF as non-aqueous solvent.  
 (a) HCl behaves as an acid and HF as a base  
 (b)  $HClO_4$  behaves as a base and HF as an acid  
 (c)  $HNO_3$  and  $H_2SO_4$  behave as base and HF as an acid  
 (d) All of the above are correct statements
40. Dipole moment and ionisation constant are maximum in case of  
 (a) HF, HF (b) HF, HI  
 (c) HI, HF (d) HI, HI
41. The tetrahedral arrangement of perchlorate ion is due to  
 (a) presence of a lone pair of electrons  
 (b) trigonal bipyramidal shape of the ion  
 (c)  $sp^3$  hybridisation  
 (d)  $sp^2$  hybridisation
42. Acid strength of oxoacids of chlorine is in order  
 (a)  $HOCl < HClO_2 < HClO_3 < HClO_4$   
 (b)  $HClO_4 < HClO_3 < HClO_2 < HOCl$   
 (c)  $HClO_3 < HClO_4 < HClO_2 < HOCl$   
 (d)  $HClO_2 < HClO_3 < HOCl < HClO_4$
43. Acid strength of oxoacids of halogen is in order  
 (a)  $HOCl > HOBr > HOI$   
 (b)  $HOI > HOBr > HOCl > HOF$   
 (c)  $HOI > HOCl > HOBr > HOF$   
 (d)  $HOCl > HOBr > HOI > HOF$
44. Which has peroxy linkage?  
 (a) Perchloric acid (b) Hypochloro acid  
 (c) Para perchloric acid (d) None of these
45.  $SO_2$  can reduce  
 (a)  $HClO_3$  to  $HCl$  (b)  $Cr_2O_7^{2-}/H^+$  to  $Cr^{3+}$   
 (c)  $MnO_4^-/H^+$  to  $Mn^{2+}$  (d) all of these
46. Bleaching powder contains  
 (a)  $CaO$  and  $Cl_2$  molecules  
 (b)  $Ca^{2+}$  and  $OCl_2^{2-}$  ions  
 (c)  $Ca^{2+}$ ,  $Cl^-$  and  $OCl^-$  ions  
 (d)  $Ca^{2+}$ ,  $O^{2-}$  ions and  $Cl_2$  molecule
47. Bleaching powder is disinfectant for purification of water when water born germs are killed. But disinfectant activity is destroyed. It is due to its disproportionation into  
 (a)  $CaCl_2$  and  $Cl_2$   
 (b)  $CaCl_2$  and  $Ca(ClO_3)_2$   
 (c)  $CaO$  and  $Cl_2$   
 (d)  $CaO$ ,  $Cl_2$  and  $CaCl_2$
48. 10 g of bleaching powder on reaction with KI required 100 mL of 1 N hypo. Thus, % of pure bleaching powder is  
 (a) 100% (b) 80%  
 (c) 63.5% (d) 35.5%
49.  $CaOCl_2 + H_2O + CO_2 \longrightarrow CaCO_3 + CaCl_2 + HOCl$   
 This reaction is simply  
 (a) oxidation  
 (b) reduction  
 (c) redox  
 (d) hydrolysis in presence of  $CO_2$
50.  $CH_3CH_2OH$  on reaction with bleaching powder forms  
 (a)  $CHCl_3$  (b)  $CCl_3CHO$   
 (c)  $CH_2ClCHO$  (d)  $CCl_4$
51.  $Cl_2O$ ,  $Br_2O$ ,  $I_2O$  have positive value of  $\Delta G$  (free energy) indicating that  
 (a) these oxides are stable  
 (b) these oxides are unstable and changes to  $X_2$  and  $O_2$   
 (c) these disproportionate into  $X^-$  and  $XO^-$   
 (d) these oxides can form interhalogen compounds
52. Select correct statement(s).  
 (a)  $Cl_2O$  and  $ClO_2$  are used as bleaching agents and as germicides  
 (b)  $I_2O_5$  is used in the quantitative estimation of CO  
 (c) Bond angle  $XOX$  varies in the order  
 $FOF < ClOCl < BrOBr$   
 (d) All of the above are correct statements
53. The bond angle in  $OF_2$  out of  $OF_2$ ,  $Cl_2O$ ,  $Br_2O$  is minimum. It is because in case of  $OF_2$   
 (a) electrons are nearer to fluorine due to high electronegativity of F compared to Cl to Br  
 (b) lone pair-lone pair repulsion decreases bond angle  
 (c) both (a) and (b) are correct  
 (d) None of the above is correct
54.  $ClO_2$  is the anhydride of  
 (a)  $HOCl$  (b)  $HClO_2$   
 (c)  $HClO_3$  (d)  $HClO_2$  and  $HClO_3$
55.  $ClO_3$  is the mixed anhydride of  
 (a)  $HClO_2$  and  $HClO_3$  (b)  $HClO_3$  and  $HClO_4$   
 (c)  $HClO_2$  and  $HClO_4$  (d)  $HClO_2$  and  $HClO_3$
56. Chlorine dioxide  
 (a) is paramagnetic in nature  
 (b) has odd-electron bond  
 (c) is stable  
 (d) has all the above properties true
57. Select incorrect statement(s).  
 (a)  $Cl_2O_6$  is diamagnetic in solid state  
 (b)  $ClO_3$  is paramagnetic and exists in liquid state  
 (c)  $Cl_2O_6$  is anhydride of  $HClO_3$   
 (d)  $ClO_3$  forms dimer due to unpaired electron

58.  $\text{Cl}_2$  gas is passed into aqueous solution of KBr and KI and  $\text{CHCl}_3$  added. It is observed that there is
- violet colour in  $\text{CHCl}_3$  layer
  - yellow colour in  $\text{CHCl}_3$  layer
  - yellow colour in aqueous layer
  - violet colour in  $\text{CHCl}_3$  layer

59. Consider following reactions in which atoms have been labelled with isotopes (indicated by \*)



In which case isotopes are equivalent in the products?

- I
  - II
  - Both I and II
  - None of these
60. In very recent Sunami in Japan, food materials were banned as they were contaminated with radioactivity. Which of the following was found to have radioactive beyond prescribed limit?
- F
  - Cl
  - I
  - At

### One or More Than One Options Correct

1. Which are correct statements?

- All halogens form oxoacids.
- All halogens show -1, +1, +3, +5, +7 oxidation states.
- Hydrofluoric acid forms  $\text{KHF}_2$  and  $\text{K}_2\text{F}_2$  and attacks glass.
- Oxidising power is in order  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

2. Select correct statement(s).

- $\text{ClO}_2$  and  $\text{Cl}_2\text{O}$  are used as bleaching agents for paper pulp and textiles
- $\text{OCl}^-$  salts are used as detergents
- $\text{OCl}^-$  disproportionates in alkaline medium
- $\text{BrO}_3^-$  is oxidised to  $\text{Br}_2$  by  $\text{Br}^-$  in acidic medium

3. In the structure of

- $\text{IF}_2^+$ , bond angle is smaller than the tetrahedral angle because of lone pair-lone pair repulsion
- $\text{IF}_4^+$ , there is  $sp^3$  hybridisation with bond angle of  $109^\circ 28'$
- $\text{IF}_6^+$ , there are six bonding electrons and no lone pairs.
- $\text{IF}_4^+$ , two F-atoms one at equatorial positions and two are inclined at an angle less than  $120^\circ$  due to lone pair-bond pair repulsion

4. In the conversion of  $\text{Br}^-$  to  $\text{BrO}_2^-$

- there is anodic oxidation in basic solution
- equivalent mass of  $\text{Br}^-$  is 20 (atomic weight of  $\text{Br} = 80$ )
- there is anodic oxidation in acidic medium
- there is cathodic reduction in basic solution

5. In the conversion of  $\text{BrO}_3^-$  to  $\text{BrO}_4^-$

- there is no change in oxidation number
- reduction takes place in basic solution
- reaction also takes place by  $\text{XeF}_2$
- equivalent mass of  $\text{BrO}_3^-$  is one-half of ionic mass

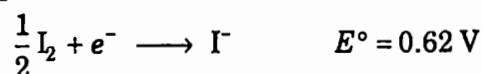
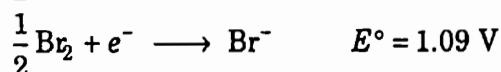
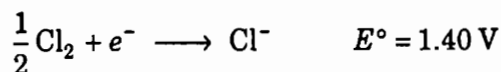
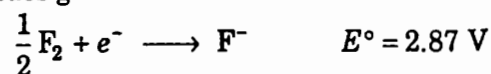
6. Select correct statement(s).

- Chile saltpetre ( $\text{NaNO}_3$ ) is a main source of  $\text{I}_2$
- $\text{IO}_3^-$  is reduced to  $\text{I}^-$  and which in turn oxidised to  $\text{I}_2$  by  $\text{IO}_3^-$  in acidic medium
- Anhydrous  $\text{HF}$  is a non-conductor of electricity
- $\text{F}_2$  is obtained by electrolysis of molten  $\text{KHF}_2$

7. Select correct statement(s).

- Colours of the halogens ( $\text{F}_2, \text{Cl}_2, \text{Br}_2, \text{I}_2$ ) in the gas phase are complimentary colours.
- Colour is due to transition of an electron from the highest occupied  $\pi^*$  molecular orbital to the lowest unoccupied  $\sigma^*$  molecular orbital
- $\text{ClO}_2$  is paramagnetic due to unpaired electrons
- $\text{ClO}_2$  dimerises to  $\text{Cl}_2\text{O}_4$  as  $\text{NO}_2$  dimerises to  $\text{N}_2\text{O}_4$

8. Base on  $E^\circ$  values gives



- Oxidising power of  $\text{F}_2$  is maximum
- Oxidising power of  $\text{I}_2$  is maximum
- Oxidising power is in order  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- Oxidising power is in order  $\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$

9.  $\text{CHCl}_3$  and  $\text{H}_2\text{O}$  form two separate immiscible layers  $\text{Br}_2$  (orange) and  $\text{I}_2$  (violet) are soluble in organic layer due to a greater extent. In test tube A ( $\text{KI} + \text{CHCl}_3 + \text{H}_2\text{O}$ ) and test tube B ( $\text{KI} + \text{KBr} + \text{CHCl}_3 + \text{H}_2\text{O}$ )  $\text{Cl}_2$  gas is passed then (based on  $E^\circ$  values in Q. 8)

- organic layer in A appear violet
- organic layer in B appear orange
- organic layer in B appear violet
- organic layer in B first appears violet then orange

10. Select correct statement(s).

- $\text{p}K_a$  value of  $\text{HI}$  (strongest halogen acid) is most negative
- high  $\text{H}-\text{F}$  bond strength makes  $\text{H}-\text{F}$  a weak acid in dilute aqueous solution
- Halogen forms clathrates by freezing solution in water
- $K_a$  values of  $\text{HX}$  is in order  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$

## Passage Comprehension Questions

### Passage 1

In the gas phase, colours of the halogens very remarkably :

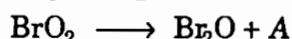
- Fluorine — Pale yellow  
Chlorine — Pale greenish-yellow  
Bromine — Deep red brown  
Iodine — Deep violet

Answer the following questions

- This colour is due to
  - transition of an electron from the highest occupies  $\pi^*$  molecular orbital to the lowest unoccupied  $\sigma^*$  molecular orbital
  - occupied  $\sigma^*$  MO to the lowest unoccupied  $\pi^*$  MO
  - Occupied  $\sigma$  MO to the lowest unoccupied  $\pi$  MO
  - None of the above
- As one moves from  $F_2$  to  $I_2$ , difference between the two energy levels
  - decreases and probability of transition increases
  - increases and probability of transition increases
  - remains unchanged and probability of transition remains unchanged
  - depends on the temperature
- Due to the above transition, absorption maximum gradually shifts from
  - red region of the visible spectrum to near UV region
  - the near UV region to the red region of the visible spectrum
  - the near UV region to the far IR region
  - the near IR region to visible region

### Passage 2

Consider following change,



$Br_2O$  and  $A$  are formed by the change of equal number oxidation number. Based on this change, answer the following questions.

- Oxide  $A$  could be
  - $Br_2O_3$
  - $Br_2O_5$
  - $Br_2O_7$
  - $BrO$
- Balanced equation is
  - $4BrO_2 \longrightarrow Br_2O + Br_2O_7$
  - $8BrO_2 \longrightarrow Br_2O + 3Br_2O_5$
  - $6BrO_2 \longrightarrow Br_2O + 2Br_2O_3$
  - None of the above
- $Br_2O$  has structure
  - $Br-Br=O$
  - $Br-O-Br$
  - $Br=O=Br$
  - None of these

4. Equivalent mass of  $Br_2$  is

- |                    |                   |
|--------------------|-------------------|
| (a) $\frac{M}{2}$  | (b) $\frac{M}{3}$ |
| (c) $\frac{2M}{3}$ | (d) $\frac{M}{6}$ |

### Passage 3

This question concerns the elements of Group 17 — fluorine, chlorine, bromine and iodine.

When sodium chloride is treated with concentrated sulphuric acid, a colourless gas,  $X$ , which fumes in moist air, is formed. When sodium iodide is treated in the same way a coloured vapour,  $Y$ , is product.

If 90% phosphoric(v) acid is used instead of sulphuric acid, a colourless gas is produced in each reaction.

1. Gases  $X$  and  $Y$  are respectively

- |                 |                 |
|-----------------|-----------------|
| (a) $Cl_2, I_2$ | (b) $HCl, I_2$  |
| (c) $HCl, HI$   | (d) $HClO, I_2$ |

2. With 90% phosphoric acid ( $H_3PO_4$ ), colourless gases formed are

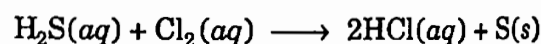
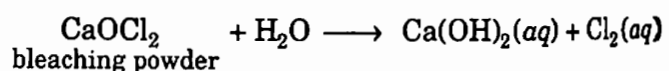
- |                |                 |
|----------------|-----------------|
| (a) $HCl, HI$  | (b) $Cl_2, I_2$ |
| (c) $HCl, I_2$ | (d) $Cl_2, HI$  |

3. Behaviour of  $H_2SO_4$  and  $H_3PO_4$  is different towards  $NaI$  because

- $H_2SO_4$  is stronger acid than  $H_3PO_4$
- $H_2SO_4$  is a strong oxidising agent and oxidises colourless gas to coloured vapour  $Y$
- $H_3PO_4$  is tribasic acid
- $H_2SO_4$  is a dibasic acid

### Passage 4

Water pollution can be by dissolved gases. Bad smell of water is due to  $H_2S$  and can be removed by treatment with bleaching powder.



Based on the above treatment answer the following questions:

- If  $H_2S$  content of contaminated water is 22 ppm by mass,  $Cl_2$  required to remove all the  $H_2S$  from 200 gallons of water (1 gallon = 3.785 L) is
  - 30.00 g
  - 71.00 g
  - 17.5 g
  - 35.00 g
- 25.0 L of a natural gas measured at  $25^\circ C$  and 740 mm Hg is bubbled through  $Pb^{2+}(aq)$ , a precipitate weighing 0.3938 g is obtained. % (ppt—parts per thousand) of  $H_2S$  by volume in the natural gas is, ( $Pb = 206$ )
  - 0.225%
  - 2.25%
  - 5.25%
  - 0.525%

## Assertion & Reason

Codes :

- (a) Both **A** and **R** are true and **R** is the correct explanation of **A**.
- (b) Both **A** and **R** are true but **R** is not the correct explanation of **A**.
- (c) **A** is true but **R** is false.
- (d) **A** is false but **R** is true.

1. **Assertion (A)** :  $\text{CaF}_2$  has been given the name fluorspar.

**Reason (R)** : Solid  $\text{CaF}_2$  emits light when heated.

2. **Assertion (A)** :  $\text{HF}$  is stored in the vessel made of wax.

**Reason (R)** :  $\text{HF}$  is a weak acid.

3. **Assertion (A)** : Fluorine has only  $-1$  oxidation state in compounds.

**Reason (R)** : Fluorine has maximum electronegativity and electron-affinity.

4. **Assertion (A)** :  $\text{Cl}_2$  or  $\text{Br}_2$  changes  $\text{KI}$  into  $\text{I}_2$  (violet in  $\text{CCl}_4$  layer),  $\text{Cl}_2$  changes  $\text{KBr}$  into  $\text{Br}_2$  (orange-yellow in  $\text{CCl}_4$  layer). Thus,  $\text{Cl}_2$  would change mixture of  $\text{KI}$  and  $\text{KBr}$  into violet layer in  $\text{CCl}_4$ .

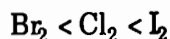
**Reason (R)** : Oxidising power is in order  $\text{I}_2 < \text{Br}_2 < \text{Cl}_2 < \text{F}_2$ .

5. **Assertion (A)** : Fluorine is not super halogen.

**Reason (R)** : It is most reactive of all the halogen.

6. **Assertion (A)** : Molten  $\text{I}_2$  is conducting in nature.

**Reason (R)** : Bond dissociation energy increases in the order



7. **Assertion (A)** : Hydrofluoric acid forms two series of salts  $\text{KHF}_2$ ,  $\text{K}_2\text{F}_2$ .

**Reason (R)** : It is a dibasic acid due to hydrogen bonding.

8. **Assertion (A)** :  $\text{CN}^-$  can be oxidised to  $(\text{CN})_2$ .

**Reason (R)** :  $\text{CN}^-$  is pseudohalide.

9. **Assertion (A)** : Bond dissociation energy of  $\text{F}_2$  is smaller than that of  $\text{Cl}_2$ .

**Reason (R)** : Bond dissociation energy is in order  $\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$ .

10. **Assertion (A)** : Aqueous solution of  $\text{NaOX}$  is alkaline.

**Reason (R)** : It is a salt of weak acid ( $\text{HOX}$ ) are strong base ( $\text{NaOH}$ ).

## True & False

- $\text{FClO}_3$  (perchloryl fluoride) has the highest dielectric constant.
- $\text{HF}$  is a weak acid but  $\text{H}^+$  ( $\text{FHF}^-$ ) is a strong acid.
- Solid  $\text{CaF}_2$  could emit light when heated.
- When  $\text{NaCl(aq)}$  is electrolysed, sodium metal is formed at the cathode and chlorine gas is formed at the anode.
- It very recent Japan Sunami, there has been increase in radioactive iodine content is salt.
- When  $\text{Cl}_2$  gas is dissolved in water, there is disproportion to  $\text{HClO}$  and  $\text{HCl}$ .
- Solid propellant in the rockets is aluminium powder with ammonium perchlorate as reducing agent.
- $\text{Br}_2$  oxidised  $\text{KCl}$  into  $\text{Cl}_2$  and  $\text{KI}$  into  $\text{I}_2$ .
- $\text{ClO}_3^+$  has structure with  $sp^2$  hybridisation having bond angle of  $120^\circ$ .
- $\text{IF}_6^+$  has regular octahedron structure.
- Interhalogen compounds are strong oxidising agents.
- Interhalogen compounds are strong reducing agents.
- $\text{X}-\text{Y}$  bond is more polar than  $\text{X}-\text{X}$  and  $\text{Y}-\text{Y}$  bonds.
- Interhalogen compounds are ionic.
- $\text{XY}_3$  types of molecules have square pyramidal structure.

## Fill in the Blanks

- $\text{FClO}_3$  is an inert and non-corrosive gas with ..... structure.
- Perchloryl fluoride ( $\text{FClO}_3$ ) is used as a rocket ..... as well as an ..... in high-voltage system.
- $\text{BrF}_3$  has ..... shaped structure.
- $\text{ClF}_3$  is a ..... in the reaction  

$$\text{ClF}_3 + \text{AsF}_3 \longrightarrow [\text{ClF}_2]^+[\text{AsF}_6]^-$$
 and is a ..... in the reaction  

$$\text{ClF}_3 + \text{NOF} \longrightarrow [\text{NO}]^+[\text{ClF}_4]^-$$
- $\text{IF}_7$  has ..... structure.
- Decreasing order of reactivity of  $\text{F}_2$ ,  $\text{ClF}$  and  $\text{ClF}_3$  is .....
- $\text{CN}$ ,  $\text{CNO}^-$ ,  $\text{CNS}^-$  are called .....
- Out of chloric acid ( $\text{HClO}_3$ ) and perchloric acid ( $\text{HClO}_4$ ) more stable is .....
- Chlorous acid is unstable and decomposes into ..... and .....

- Ammonium perchlorate is used as the ..... in the solid booster rockets for the space shuttle.
- ..... displaces three halogens from their compounds.
- $\text{Cl}^-$  can be oxidised by .....
- $\text{Br}_2$  can be reduced by .....
- Fluorine and ..... can oxidise water to oxygen.
- Oxidation of ..... and ..... by  $\text{Cl}_2$  will give  $\text{Br}_2$  and  $\text{I}_2$  respectively.

## Matrix-Match Type Questions

### I. One or More Correct

- Match the oxides in Column I with their corresponding properties in Column II.

| Column I                   | Column II                        |
|----------------------------|----------------------------------|
| A. $\text{Cl}_2\text{O}$   | 1. Anhydride of $\text{HOCl}$    |
| B. $\text{ClO}_2$          | 2. Anhydride of $\text{HClO}_2$  |
| C. $\text{Cl}_2\text{O}_6$ | 3. Anhydride of $\text{HClO}_3$  |
| D. $\text{Cl}_2\text{O}_7$ | 4. Anhydride of $\text{HClO}_4$  |
|                            | 5. $sp^3$ hybridization          |
|                            | 6. Paramagnetic in gaseous state |
|                            | 7. Paramagnetic in liquid state  |

- Match the species in Column I with the corresponding properties in Column II.

| Column I         | Column II                                                       |
|------------------|-----------------------------------------------------------------|
| A. $\text{SO}_2$ | 1. Turns lime water milky                                       |
| B. $\text{CO}_2$ | 2. Turns $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$ solution green |
| C. $\text{Cl}_2$ | 3. Turns $\text{KI}/\text{starch}$ blue                         |
| D. $\text{Br}_2$ | 4. Disinfectant for drinking water                              |
| E. $\text{O}_3$  | 5. Green house effect                                           |
|                  | 6. Acid rain                                                    |
|                  | 7. Controls pH of blood                                         |

## Integer Answer Types

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the ORS have to be darkened. For example, if the correct answers to question number X, Y, Z and W (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will like the following

| X | Y | Z | W |
|---|---|---|---|
| ① | ① | ① | ① |
| ② | ② | ② | ② |
| ③ | ③ | ③ | ③ |
| ④ | ④ | ④ | ④ |
| ⑤ | ⑤ | ⑤ | ⑤ |
| ⑥ | ⑥ | ⑥ | ⑥ |
| ⑦ | ⑦ | ⑦ | ⑦ |
| ⑧ | ⑧ | ⑧ | ⑧ |
| ⑨ | ⑨ | ⑨ | ⑨ |

### Set I

- $^{35}_{17}\text{Cl}$  and  $^{37}_{17}\text{Cl}$  are two isotopes of chlorine in mass ratio of 3 : x where x = .....
- $\text{CaOCl}_2$  (bleaching powder) has two types of chlorine with different oxidation numbers. Sum of oxidation number is .....
- Number of series of salts formed by hydrofluoric acid is .....
- $\text{Cl}_2$  disproportionates to  $\text{Cl}^-$  and species A such that equivalent mass of  $\text{Cl}_2$  is 71. Thus, oxidation number of chlorine in species A is .....
- Number of electrons forming bond between Cl and O is  $\text{ClO}_2$  is .....
- Maximum acidic character is shown by the oxyacids of halogens with oxidation number of halogens as .....
- $\text{Br}^-$  and  $\text{BrO}_x^-$  in acidic medium forms  $\text{Br}_2$  where x = .....
- $3\text{Cl}_2 + x\text{NaOH} \longrightarrow \text{NaCl} + \text{NaClO}_3$ . x is .....

### Set II

- How many lone-pairs and bond-pairs are present in  $\text{IF}_7$  ?
- How many lone-pairs are present in  $\text{CH}_3$  ?
- $\text{ClO}_2$  has odd-electron bonds. How many electrons are involved in (Cl—O) bond?
- $\text{ClO}_2$  is paramagnetic due to ..... unpaired electron(s).
- How many of the following have underlined atoms in different oxidation states?  
 $\text{K}_2\text{Hg}\underline{\text{I}}_4$ ,  $\text{CaO}\underline{\text{Cl}}_2$ ,  $\text{Na}_2\underline{\text{S}}_2\text{O}_3$ ,  $\text{Na}_2\underline{\text{S}}_4\text{O}_6$ ,  $\text{H}_2\underline{\text{S}}\text{O}_5$ ,  $\text{H}_2\underline{\text{S}}_2\underline{\text{O}}_8$ ,  $\text{Cr}\underline{\text{O}}_5$ ,  $\underline{\text{I}}_3^-$
- How many of the following have Cl atom in  $sp^3$  hybridised state?  
 $\text{ClO}_2$ ,  $\text{Cl}_2\text{O}$ ,  $\text{Cl}_2\text{O}_7$ ,  $\text{Cl}_2\text{O}_6$ ,  $\text{ClO}_4^-$
- How many of the are water insoluble?  
 $\text{AgF}$ ,  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{CaF}_2$ ,  $\text{BaSO}_4$
- 6.35 g of impure bleaching powder paste is mixed with  $\text{KI}$  and  $\text{I}_3^-$  formed required 50 mL of 0.1 M hypo in neutral medium. Thus % purity of bleaching powder is .....

# Answers & Solutions

## Master Exercises

### Exercise 1

#### Short Answer Type Questions

- $$\text{Br}^- \longrightarrow \frac{1}{2}\text{Br}_2 + e^-$$

$$65 \times 10^{-3} \text{ g Br}^- = 32.5 \times 10^{-3} \text{ g Br}_2 \text{ is in } 1 \text{ dm}^3$$

$$\therefore 1000 \text{ g Br}_2 \text{ is in } = \frac{1000}{32.5 \times 10^{-3}} = 30769 \text{ dm}^3$$
- $$\text{(a) } \text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\underset{\text{I}}{\text{CH}_2} \text{ (ICl} \longrightarrow \text{I}^+ + \text{Cl}^-)$$

$$\text{(b) } 3\text{Cl}_2 + 6\text{NaOH} \longrightarrow 3\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$$

$$\text{(c) } \text{Cl}_2 + \text{S}^{2-} \longrightarrow 2\text{Cl}^- + \text{S}$$

$$\text{(d) } \text{SO}_2 + \text{I}_2 + 2\text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + 2\text{HI}$$

$$\text{(e) } \text{SnCl}_2 + 2\text{HCl} + \text{I}_2 \longrightarrow \text{SnCl}_4 + 2\text{HI}$$
- $\text{I}^- \rightarrow \text{I}_2$ ;  $\text{I}^-$  behaves as a Lewis base.
- If acid is strong, its conjugate base is weak and vice-versa.  
 (a)  $\text{ClO}_2^-$  (b)  $\text{OH}^-$  (c)  $\text{Cl}^-$  (d)  $\text{CH}_3\text{CH}_2^-$  (e)  $\text{NO}_2^-$   
 (f) almost same
- $$\text{I}_2\text{O}_5 + 5\text{CO} \longrightarrow \text{I}_2 + 5\text{CO}_2$$
 $\text{I}_2\text{O}_5$  is reduced to  $\text{I}_2$ , CO is oxidised to  $\text{CO}_2$
- $$2\text{Ca}(\text{OCl})\text{Cl} + \text{H}_2\text{O} + \text{CO}_2 \longrightarrow \text{CaCl}_2 + \text{CaCO}_3 + 2\text{HOCl}$$
- $\text{Cl}_2\text{O}_6$  has paired electrons. In liquid state or in aqueous solution Cl—Cl bond breaks giving one unpaired electron hence, diamagnetic nature of  $\text{Cl}_2\text{O}_6$  changes to paramagnetic nature in  $\text{ClO}_3$ .
 

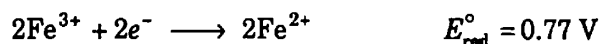
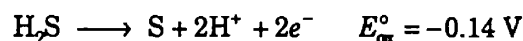
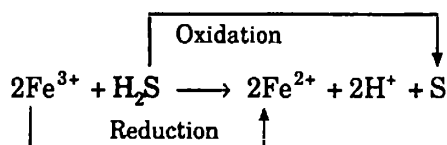
$$\begin{array}{c} \text{O} \quad \text{O} \\ | \quad | \\ \text{O}-\text{Cl}-\text{Cl}-\text{O} \\ | \quad | \\ \text{O} \quad \text{O} \end{array}$$

$$\begin{array}{c} \text{O} \\ | \\ \text{O}-\text{Cl}^\bullet \\ | \\ \text{O} \end{array}$$
- (A):  $\text{Cl}_2$  (B):  $\text{AgCl}$  (C):  $\text{ClO}_2$  (D):  $\text{O}_2$  (E):  $\text{KClO}_2$   
 (F):  $\text{KClO}_3$ .
- (a) chlorine (b) iodine (c) fluorine (d) iodine  
 (e) chlorine
- $\longrightarrow \text{BIF}$   
 $\longrightarrow \text{HCl} + \text{HOCl}$   
 $\longrightarrow 2\text{HCl} + \text{S}$

- (a) hypochlorous acid +1  
 (b) chlorous acid +3  
 (c) hypobromous acid +1  
 (d) bromic acid +5  
 (e) periodic acid +7  
 (f) perchloric acid +7

#### Analytical Questions

- (i) Oxidation of  $\text{H}_2\text{S}$  by  $\text{Fe}^{3+}$  can be written as

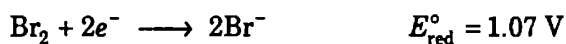
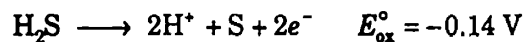
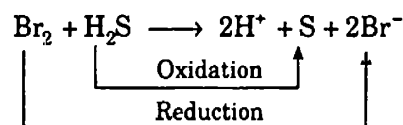


$$\text{Thus, } E_{\text{cell}}^\circ = 0.63 \text{ V}$$

$$\text{Thus, } \Delta G^\circ = -nFE_{\text{cell}}^\circ = -\text{ve.}$$

Thus, oxidation of  $\text{H}_2\text{S}$  by  $\text{Fe}^{3+}$  is spontaneous.

- (ii) Oxidation of  $\text{H}_2\text{S}$  by  $\text{Br}_2$  can be written as



$$\text{Thus, } E_{\text{cell}}^\circ = 0.93 \text{ V}$$

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ = -\text{ve}$$

Hence, oxidation of  $\text{H}_2\text{S}$  by  $\text{Br}_2$  is spontaneous.

- Refer text

- Solution in *n*-hexane contains uncomplexed  $\text{I}_2$  molecule; charge-transfer complex formed with benzene; probably O— and N—donor complexes with ethanol and pyridine; pyridine complex being the most stable.

## Exercise 2

### Only One Option Correct

- |         |         |         |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c)  | 2. (b)  | 3. (a)  | 4. (b)  | 5. (a)  | 6. (b)  | 7. (a)  | 8. (a)  | 9. (d)  | 10. (b) |
| 11. (a) | 12. (a) | 13. (d) | 14. (a) | 15. (c) | 16. (c) | 17. (d) | 18. (a) | 19. (d) | 20. (b) |
| 21. (d) | 22. (d) | 23. (a) | 24. (b) | 25. (b) | 26. (b) | 27. (d) | 28. (b) | 29. (c) | 30. (d) |
| 31. (a) | 32. (d) | 33. (c) | 34. (a) | 35. (b) | 36. (a) | 37. (b) | 38. (c) | 39. (c) | 40. (b) |
| 41. (c) | 42. (a) | 43. (b) | 44. (d) | 45. (d) | 46. (c) | 47. (b) | 48. (c) | 49. (d) | 50. (a) |
| 51. (b) | 52. (d) | 53. (a) | 54. (d) | 55. (b) | 56. (d) | 57. (c) | 58. (a) | 59. (b) | 60. (c) |

### One or More Than One Options Correct

1. (c,d)    2. (a,c,d)    3. (a,c,d)    4. (a,b)  
 5. (a,b,c,d)    6. (a,b,c,d)    7. (a,b,c)    8. (a,c)  
 9. (a,c)    10. (a,b,c,d)

### Passage Comprehension Questions

#### Passage 1

1. (a)    2. (a)    3. (b)

#### Passage 2

1. (c)    2. (a)    3. (b)    4. (c)

#### Passage 3

1. (b)    2. (a)    3. (b)

#### Passage 4

1. (d)    2. (b)

### Assertion & Reason

1. (a) fluorspar name is given after fluorescence (meaning emitting light)  
 2. (b)  
 3. (c) Cl has maximum electron-affinity  
 4. (a)  $\text{Cl}_2$  oxidises  $\text{Br}^-$  to  $\text{Br}_2$ , and  $\text{Br}_2$  oxidises  $\text{I}^-$  to  $\text{I}_2$  (violet)  
 5. (a)  $\text{I}^+$  and  $\text{I}_3^-$  are formed, order is  $\text{Cl}_2 < \text{Br}_2 < \text{I}_2$   
 6. (c)    7. (a)    8. (b)    9. (c)    10. (b)

### True & False

1. T    2. T    3. T    4. F    5. T    6. T  
 7. F    8. F    9. T    10. T    11. T    12. F  
 13. T    14. F    15. F

### Fill in the Blanks

1. tetrahedral    2. propellant, insulator    3. T  
 4. Lewis base, Lewis acid  
 5. pentagonal bipyramidal structure  
 6.  $\text{ClF}_3 > \text{ClF} > \text{F}_2$     7. pseudohalides    8.  $\text{HClO}_4$

9.  $\text{HCl}$ ,  $\text{ClO}_2$     10. oxidises    11.  $\text{F}_2$     12.  $\text{F}_2$   
 13.  $\text{I}^-$     14. chlorine    15.  $\text{Br}^-$ ,  $\text{I}^-$

### Matrix-Match Type Questions

#### I. One or More Correct

1. (A) — (1,5);    (B) — (2,3,5,6);    (C) — (3,4,5,7);  
 (D) — (4,5)  
 2. (A) — (1,2,6);    (B) — (1,5,7);    (C) — (3,4);  
 (D) — (3);    (E) — (3,4)

### Integer Answer Types

#### Set I

|             |   |   |   |   |   |   |   |   |
|-------------|---|---|---|---|---|---|---|---|
| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Answers →   | 1 | 0 | 2 | 1 | 3 | 7 | 3 | 6 |
|             | ① | ① | ① | ① | ① | ① | ① | ① |
|             | ② | ② | ② | ② | ② | ② | ② | ② |
|             | ③ | ③ | ③ | ③ | ③ | ③ | ③ | ③ |
|             | ④ | ④ | ④ | ④ | ④ | ④ | ④ | ④ |
|             | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ |
|             | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ |
|             | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ |
|             | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ |
|             | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ |

#### Set II

|             |   |   |   |   |   |   |   |   |
|-------------|---|---|---|---|---|---|---|---|
| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Answers →   | 7 | 2 | 3 | 1 | 6 | 5 | 5 | 5 |
|             | ① | ① | ① | ① | ① | ① | ① | ① |
|             | ② | ② | ② | ② | ② | ② | ② | ② |
|             | ③ | ③ | ③ | ③ | ③ | ③ | ③ | ③ |
|             | ④ | ④ | ④ | ④ | ④ | ④ | ④ | ④ |
|             | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ |
|             | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ |
|             | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ |
|             | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ |
|             | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ |

# The Transition and Inner Transition Elements

"If elements of s- and p-blocks make two hands of the Periodic Table, then elements of d- and f-blocks are its heart and kidney"

## Quick Points

- Electrons in various subshells of a given shell are filled based on Aufbau rule (ascending energy rule) and last filling electron decides block.
- Chemical reactivity is based on the position of the element in electrochemical series (ECS). A particular electrochemical reaction is possible of reducing agent in ECS is above oxidising agent, i.e., more negative value of standard reduction potential ( $E_{M^{n+}/M}^{\circ}$ ) indicates the better reducing nature of the metal.

- Equivalent mass in a redox reaction

$$= \frac{\text{molar mass}}{\text{change in oxidation number}}$$

$$= \frac{\text{molar mass}}{\text{electrons exchanged in a redox reaction}}$$

Thus, for  $(\text{MnO}_4^- \xrightarrow{+5e^-} \text{Mn}^{2+})$

$$\text{Equivalent mass of MnO}_4^- = \frac{\text{molar mass}}{5}$$

and for,  $(\text{Cr}_2\text{O}_7^{2-} \xrightarrow{+6e^-} 2\text{Cr}^{3+})$

$$\text{Equivalent mass of Cr}_2\text{O}_7^{2-} = \frac{\text{molar mass}}{6}$$

## Learning Framework of the Chapter

- Transition Elements (d-Block)
- Physical Properties
- Compounds
- Inner-Transition Elements (f-Block)



## Transition Elements (*d*-Block)

| Group  | III B | IV B | V B | VI B | VII B | VIII B |    |    | I B | II B |
|--------|-------|------|-----|------|-------|--------|----|----|-----|------|
|        | 3     | 4    | 5   | 6    | 7     | 8      | 9  | 10 | 11  | 12   |
| Period |       |      |     |      |       |        |    |    |     |      |
| 4th    | Sc    | Ti   | V   | Cr   | Mn    | Fe     | Co | Ni | Cu  | Zn   |
| 5th    | Y     | Zr   | Nb  | Mo   | Tc    | Ru     | Rh | Pd | Ag  | Cd   |
| 6th    | La    | Hf   | Ta  | W    | Re    | Os     | Ir | Pt | Au  | Hg   |
| 7th    | Ac    | Rf   | Lu  | Sg   | Bh    | Hs     | Mt | Ds |     |      |

On August 16, 2003 IUPAC approved the name for the element of atomic number 110, as **DARMSTADIUM** with symbol Ds. It is a super heavy element which was first produced in 1994

## Physical Properties

As discussed in the **Periodicity**, three series of elements are formed by filling the *3d*, *4d* and *5d*-shells of electrons. Together these comprise the *d*-block elements. They are often called **transition elements** because their position in the Periodic Table is between the *s*-block and *p*-block elements. The electrons are added to the *penultimate shell*, expanding it from 8 to 18 electrons.

### DEEP Focus

Thus, transition metals typically have incompletely filled *d*-subshells or readily give rise to ions with incompletely *d*-subshells. The group 12 (II B) metals—Zn, Cd and Hg do not have this characteristic electron configuration, and so although they are sometimes called transition metals, they really do not belong in this category.

- The elements with a partially filled *f*-subshell in common oxidation states are known as ***f*-block transition elements** or **inner-transition elements**. They are the two rows elements at the bottom of the Periodic Table. The elements in the first row are called the **lanthanides or rare earths**. The elements in the second row are called **actinides**. All of the actinides are radioactive, and from neptunium (*Z* = 93) onwards, are synthetic. They have been produced in nuclear reactor or by using particle accelerators.
- The lowest-energy configuration of the lutetium atom is [Xe]  $4f^{14} 5d^1 6s^2$ , and in its only common oxidation state (+3), the configuration is [Xe]  $4f^{14}$ . Although both configurations have a filled *f*-subshell, lutetium is usually considered a lanthanide element.

### DEEP Focus

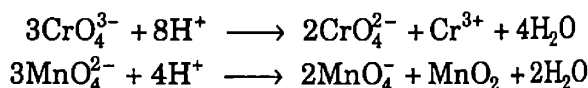
- Nuclear charge increases from Sc to Cu, but electrons are being added to the inner *3d*-subshell. These *3d* electrons shield the *4s*-electrons from the increasing nuclear charge somewhat more effectively than outer-shell electrons can shield one another, hence the atomic radii decrease less rapidly. For the same reason, electronegativities and ionisation energies increase only slightly from Sc across to Cu compared with the increase from Na to Ar.

Physical properties of *3d*-series [Sc(21)—Zn(30)] have been summarised in Table 16.1.

## Comparison of the First Row Transition Metals Through the *d*-Electron Configuration

**The *d*<sup>0</sup> configuration** Of the simple ions, only Sc<sup>3+</sup> is known to have this configuration. This configuration then occurs for those metals in which the formal oxidation states equal the total number of *3d* and *4s*-electron. This is true for Ti(IV), V(V), Cr(VI), and Mn(VII) but for Fe(VIII) is unknown.

**The *d*<sup>1</sup> configuration** Except vanadium(IV), all others with this configuration are either reducing or undergo disproportionation. For example, disproportionation occurs for Cr(V) and Mn(VI) as follows:



**The *d*<sup>2</sup> configuration** This configuration ranges from Ti<sup>II</sup> which is very strongly reducing, to Fe<sup>VI</sup>, which is very strongly oxidising. Vanadium (III) is also reducing.

**The *d*<sup>3</sup> configuration** Chromium (III) is the important species with this configuration which is stable and well known for complex formation. In other cases, this configuration is relatively unimportant.

**The *d*<sup>4</sup> configuration** There are really no stable species with this configuration. The chromium (II) is strongly reducing and manganese(III) disproportionates.

**The *d*<sup>5</sup> configuration** The two important species with this configuration are Mn<sup>2+</sup> and Fe<sup>3+</sup>, the latter may, however, be reduced to Fe<sup>2+</sup>.

**The *d*<sup>6</sup> configuration** Iron(II) and cobalt(III) are important species with this configuration. Iron(II) is quite stable although a mild reducing agent and cobalt(III) is stable in the presence of strong complexing reagents.

**The *d*<sup>7</sup> configuration** The species with this configuration is cobalt(II) which is stable in aqueous solutions but gets oxidised to form Co(III) complexes in the presence of strong ligands.

**The *d*<sup>8</sup> configuration** Nickel(II) is the most important species with this configuration.

**The  $d^9$  configuration** The configuration is found in  $\text{Cu}^{2+}$  compounds and is by far the most important in the chemistry of copper. Otherwise, this configuration is of little importance.

**The  $d^{10}$  configuration** The two species  $\text{Cu}^+$  and  $\text{Zn}^{2+}$  are important with this configuration. Whereas, copper(I) is easily oxidised to copper(II), zinc(II) is the only state known for zinc.

## Metallic Character

Nearly all the transition metals have the simple hcp, ccp or bcc lattice characteristics of true metals. They have relatively high densities. They are malleable, ductile and have high tensile strength, thermal and electrical conductivity and lustre. Melting points of 3d-series (shown in Fig. 16.1) rise to a maximum and fall as the atomic number increases except in Mn where melting point is minimum. **High melting point and high heat of atomisation indicate that the atoms in these elements are held together by strong metallic bonds that are present in the molten states as well. Greater the number of valence shell, stronger is the resultant bonding.**

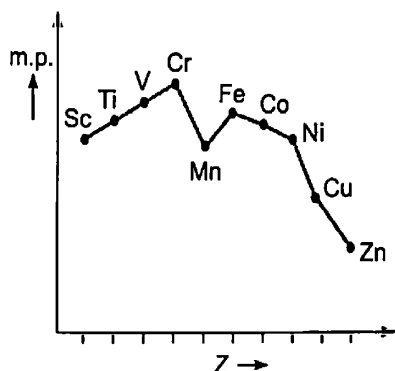


Fig. 16.1 Melting point of 3d-series elements (not according to scale)

The periodic trends in the boiling points are similar to those in the melting points. As the process of boiling requires almost complete breaking of bonds and such metallic bonding exists in the liquid state to some extent, high temperatures are necessary. Therefore, the boiling points of metals are much higher than their melting points.

## Oxidation States

A characteristic property of the d-transition metals is their ability to exhibit several oxidation states differing usually by units of one. **This is due to the fact that  $(n-1)d$  electrons may get involved along with ns-electrons in bonding, as electrons in  $(n-1)d$  orbitals are in an energy state comparable to ns-electrons.** The stability of a given oxidation state depends on the nature of the element with which the transition metal is combined. **The highest oxidation states are found in the compounds of fluorides and**

**oxides because of most electronegative nature of F and O.** The different oxidation states of 3d-series have been given below (very rare oxidation states are provided in parenthesis).

| Sc   | Ti   | V   | Cr  | Mn    | Fe   | Co   | Ni    | Cu    | Zn |
|------|------|-----|-----|-------|------|------|-------|-------|----|
|      |      |     | I   |       |      |      |       | I     |    |
| (II) | (II) | II  | II  | II    | II   | II   | II    | II    | II |
| III  | III  | III | III | (III) | III  | III  | (III) | (III) |    |
|      | IV   | IV  | IV  | IV    | (IV) | (IV) | (IV)  |       |    |
|      |      | V   | (V) | (V)   | (V)  | (V)  |       |       |    |
|      |      |     | VI  | VI    | VI   |      |       |       |    |
|      |      |     |     | VII   |      |      |       |       |    |

- The lesser number of oxidation states in the beginning of the series can be due to the presence of too few electrons to loose or share, towards the end of the series it can be ascribed to the presence of too many electrons and thus fewer empty orbitals to share electrons with the ligands.
- Except Sc, the most common oxidation state of the first row transition elements is II which arises from the loss of two 4s-electron. This means that after Sc, d-orbitals become more stable than the s-orbital.
- In the II and III oxidation states, bonds formed are mostly ionic. In compounds of the higher oxidation states, the bonds are formed by the removal or sharing of d-electron hence, the bonds formed are essentially covalent (as in  $\text{MnO}_4^-$ ).
- Within a group, the maximum oxidation state increases with atomic numbers.
 

|        |                       |
|--------|-----------------------|
| Fe     | II, III               |
| Ru, Os | II, III, IV, VI, VIII |
- Transition metals also form compounds in low oxidation states (1,0). Such compounds are expected to be unstable except in cases where vacant d-orbitals are used for accepting lone-pairs from  $\pi$ -bonding ligands e.g.,  $\text{Ni}(\text{CO})_4$ ,  $[\text{Ag}(\text{CN})_2]^-$ ,  $[\text{Ag}(\text{NH}_3)_2]^+$ .

## DEEP Focus

- When an element exists in more than one oxidation state, standard electrode potential data provide a clue to the relative stabilities of different states w.r.t. oxidation.  $\text{Cr}^{2+}$  is unstable in water w.r.t. oxidation whereas  $\text{Cr}^{3+}$  is stable in water;  $\text{Fe}^{2+}$  is unstable in aerated water (and changes to  $\text{Fe}^{3+}$ ) w.r.t. oxidation.
- Another feature is the reduced tendency of higher oxidation states towards the end of the series. This could be due to steady increase in the effective nuclear charge along the series thus pulling the d-orbitals into the electron core and not making them readily available for bonding. Thus, only oxidation of zinc is  $\text{Zn}(\text{II})$  where no d-orbital is involved. Also, it is difficult to form species that do not utilise the d-electrons, i.e., Sc(II) is virtually unknown and Ti(IV) is more stable than Ti(II).

Table 16.1 Selected Properties of Elements of the First Transition Series

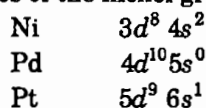
| Properties                                             | Sc (21)                                   | Ti (22)                         | V (23)                          | Cr (24)                         | Mn (25)                         | Fe (26)                         | Co (27)                         | Ni (28)                         | Cu (29)                          | Zn (30)                          |
|--------------------------------------------------------|-------------------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|----------------------------------|----------------------------------|
| Electron configuration                                 | [Ar] 3d <sup>1</sup> 4s <sup>2</sup>      | 3d <sup>2</sup> 4s <sup>2</sup> | 3d <sup>3</sup> 4s <sup>2</sup> | 3d <sup>5</sup> 4s <sup>1</sup> | 3d <sup>5</sup> 4s <sup>2</sup> | 3d <sup>6</sup> 4s <sup>2</sup> | 3d <sup>7</sup> 4s <sup>2</sup> | 3d <sup>8</sup> 4s <sup>2</sup> | 3d <sup>10</sup> 4s <sup>1</sup> | 3d <sup>10</sup> 4s <sup>2</sup> |
| Radius/pm                                              | 161                                       | 145                             | 132                             | 127                             | 124                             | 124                             | 125                             | 125                             | 128                              | 133                              |
| M <sup>+</sup>                                         | —                                         | 90                              | 88                              | 85                              | 80                              | 77                              | 75                              | 69                              | 72                               | —                                |
| M <sup>2+</sup>                                        | 81                                        | 77                              | 74                              | 64                              | 66                              | 60                              | 64                              | —                               | —                                | 74                               |
| Covalent radius/pm                                     | 144                                       | 132                             | 122                             | 117                             | 117                             | 117                             | 116                             | 115                             | 117                              | 125                              |
| (IE) <sub>1</sub>                                      | 631                                       | 656                             | 650                             | 652                             | 717                             | 762                             | 758                             | 736                             | 775                              | 906                              |
| (IE) <sub>2</sub>                                      | 1235                                      | 1309                            | 1413                            | 1591                            | 1509                            | 1561                            | 1645                            | 1751                            | 1958                             | 1733                             |
| (IE) <sub>3</sub>                                      | 2389                                      | 2650                            | 2828                            | 2986                            | 3250                            | 2956                            | 3231                            | 3393                            | 3578                             | 3833                             |
| Abundance ppm by weight                                | 25                                        | 6320                            | 136                             | 122                             | 1060                            | 60000                           | 29                              | 99                              | 68                               | 76                               |
| Melting point/°C                                       | 1397                                      | 1672                            | 1710                            | 1900                            | 1244                            | 1530                            | 1495                            | 1455                            | 1083                             | 420                              |
| E° <sub>M<sup>2+</sup>/M/V</sub>                       | -2.08                                     | -1.63                           | -1.18                           | -0.91                           | -1.19                           | -0.44                           | -0.28                           | -0.23                           | -0.34                            | -0.76                            |
|                                                        | (Sc <sup>3+</sup> + 3e <sup>-</sup> → Sc) |                                 |                                 |                                 |                                 |                                 |                                 |                                 |                                  |                                  |
| Density g/cm <sup>3</sup>                              | 2.99                                      | 4.49                            | 5.96                            | 7.20                            | 7.20                            | 7.86                            | 8.90                            | 8.91                            | 8.92                             | 7.14                             |
| Electrical conductivity [w.r.t. Ag which is 100 (say)] | —                                         | 2                               | 3                               | 10                              | 2                               | 17                              | 24                              | 24                              | 97                               | 100                              |
| Common oxidation state                                 | +3                                        | +4                              | +3                              | +3                              | +2                              | +2                              | +2                              | +2                              | +1                               | +2                               |
|                                                        |                                           |                                 | +4                              | +6                              | +4                              | +3                              | +3                              |                                 | +2                               |                                  |
|                                                        |                                           |                                 | +5                              |                                 | +7                              |                                 |                                 |                                 |                                  |                                  |
| Sublimation energy/kJ mol <sup>-1</sup>                | 305                                       | 429                             | 459                             | 349                             | 220                             | 351                             | 382                             | 372                             | 305                              | 115                              |
| Electronegativity (A/R)                                | 1.20                                      | 1.30                            | 1.45                            | 1.55                            | 1.60                            | 1.65                            | 1.70                            | 1.75                            | 1.75                             | 1.65                             |

Table 16.2 Reactivity of Some Oxidation States of 3d-series Elements in Aqueous Solution

| Reducing agent                      | Most stable      | Oxidising agents                                                                                             |
|-------------------------------------|------------------|--------------------------------------------------------------------------------------------------------------|
| —                                   | Sc <sup>3+</sup> | —                                                                                                            |
| Ti <sup>2+</sup> , Ti <sup>3+</sup> | Ti <sup>3+</sup> | —                                                                                                            |
| V <sup>2+</sup> , V <sup>3+</sup>   | V <sup>4+</sup>  | V <sup>5+</sup>                                                                                              |
| Cr <sup>2+</sup>                    | Cr <sup>3+</sup> | Cr <sup>6+</sup> (CrO <sub>4</sub> <sup>2-</sup> )                                                           |
| —                                   | Mn <sup>2+</sup> | Mn <sup>3+</sup> , Mn <sup>4+</sup> (MnO <sub>2</sub> )<br>Mn <sup>7+</sup> (MnO <sub>4</sub> <sup>-</sup> ) |
| Fe <sup>2+</sup>                    | Fe <sup>3+</sup> | —                                                                                                            |
| —                                   | Co <sup>2+</sup> | Co <sup>3+</sup>                                                                                             |
| —                                   | Ni <sup>2+</sup> | —                                                                                                            |
| Cu <sup>+</sup>                     | Cu <sup>2+</sup> | —                                                                                                            |

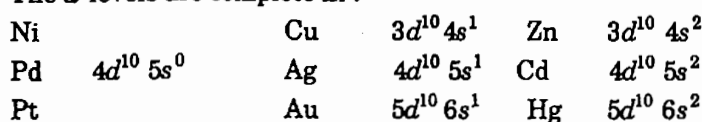
### DEEP Focus

- The electronic structure of the atoms in the second and third rows do not always follow the pattern of the first row. The structures of the nickel group are :



Since a full shell of electrons is a stable arrangement, the place where this occurs is of importance.

The *d*-levels are complete in :



Even though the ground state of the atom has a *d*<sup>10</sup>-configuration, Pd and the coinage metals Cu, Ag and Au behave as typical transition elements. This is because in their most common oxidation states, Cu (II) has a *d*<sup>9</sup>-configuration, and Pd (II) and Au (III) have *d*<sup>8</sup>-configuration (incomplete *d* level). However, Zn (II), Cd (II) and Hg (II) have a *d*<sup>10</sup> configuration. Because of this, these elements do not show the properties characteristic of transition elements.

### Ionisation Energies

- The magnitude of ionisation energies provide an indication of the energy needed to raise the metal to a particular oxidation state in a compound.
- (IE)<sub>1</sub> of 5*d*-elements are higher than those of the 3*d* and 4*d*-elements. This is due to greater effective nuclear charge acting on outer valence electrons because of the weak shielding of the nucleus by 4*f*-electrons. The ionisation energies of the 3*d* and 4*d*-elements are irregular.

### DEEP Focus

- It is important to note that though the 4*s*-orbitals are occupied before 3*d*-orbitals, we cannot say that they are always more stable. In fact, the ionisation of transition elements takes place by the loss of *ns*-electrons first. What happens actually is that when the electron is ionised from any transition element, say from iron (*Z* = 26) of 3*d*-series, the effective nuclear charge experienced by the 3*d*-electrons

is greatly enhanced over that of any 4s-electron as a direct consequence of the greater stability attained by the 3d-orbitals. Thus, 3d-orbitals are expected to drop in energy below 4s-orbitals. Thus, ionisation of two or more electrons from an atom of a transition element will take place with the removal of s-electrons in preference to the d-electrons.

- Common oxidation states for each element include +2 and +3 or both. The +3 oxidation states are more stable at the beginning of the series, whereas towards the end of +2 oxidation states are more stable. This can be explained by study of variation of (IE) plots. IE increases gradually from left to right. However, the third (IE), when an electron is removed from 3d-orbital, increases more rapidly than the second and third (IE). Because it takes more energy to remove the third electron from the metals near the end of the row than from those near the beginning, the metals near the end tend to form  $M^{2+}$  ions rather than  $M^{3+}$  ions. (Fig. 16.2)

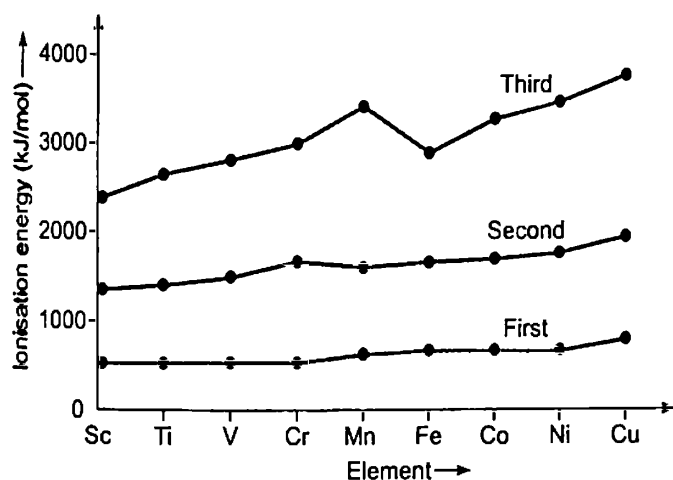


Fig. 16.2 Variation of the first, second, and third ionisation energies for the first transition metals.

### DEEP Focus

- It is possible to determine thermodynamic stability of the transition metal compounds based on the values of (IE) of the metals.  $(IE)_1$ ,  $(IE)_2$ ,  $(IE)_3$  and  $(IE)_4$  of Ni and Pt in  $\text{kJ mol}^{-1}$  are compared.

|    | $(IE)_1 + (IE)_2$ | $(IE)_3 + (IE)_4$ | Total |
|----|-------------------|-------------------|-------|
| Ni | 2.49              | 8.80              | 11.29 |
| Pt | 2.66              | 6.70              | 9.36  |

Thus, nickel (II) compounds tend to be thermodynamically more stable than platinum (II) while platinum (IV) compounds are relatively more stable than nickel (IV).

$\text{K}_2\text{PtCl}_6$  is well known but such type of nickel compound is not formed. Following factors also decide the stability of the compounds :

- the energy of the sublimation,
- the lattice energy,
- the solvation energy.

## Electrode Potential

When a metal is placed in a solution of its ions a potential difference is set up between the metal and the solution. There is a tendency for the metal ions to leave the metal lattice and go into the solution thus leaving an excess of electrons and hence a negative charge on the metal; there is also a reverse tendency for the metal ions from the solution to deposit on the metal leading to a positive charge on the metal. In practice one of these effects is greater than the other, bringing about a potential difference between the metal and the solution. The value of this potential difference for a particular metal depends upon the nature of metal, the concentration of the metal ions in solution and the temperature. **By convention, the potential difference set up in a 1 M solution of metal ions at 298 K is called the standard electrode potential.** (measured w.r.t. to reference half-cell)

In general, we can say that more negative the value of the electrode potential for the couple  $M^{n+}/M$ , more is the reducing power of the element. Similarly, more positive is the value of electrode potential for the couple  $M^{n+}/M$ , more is the oxidising power of the element. The values of some standard electrode potentials for the elements of first transition series are given in Table 16.1. Electrode potential is a measure of the electropositive character and the reactivity of the metals. In general along a period, there is a decrease in electropositive character. The reactivity of metals also decreases along a period and down a group. All the elements of the first transition series, except copper, have negative values and can react with acids ( $\text{H}^+$ ) producing hydrogen. A plot of variation of the electrode potential of the transition elements of 3d-series is shown in Fig. 16.3.

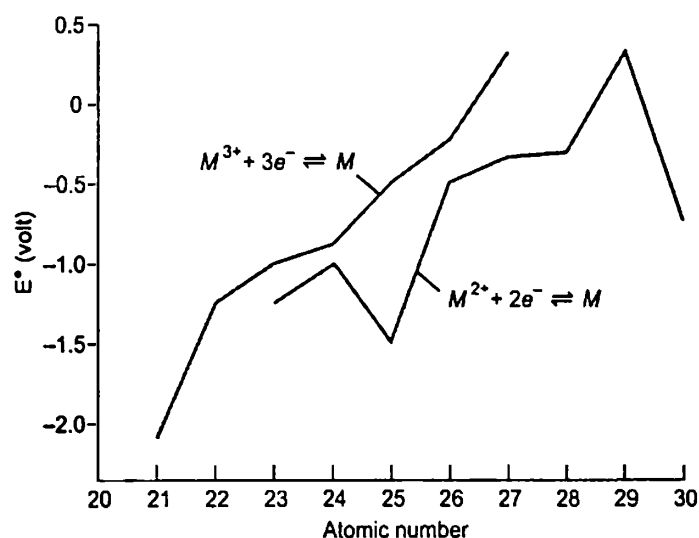
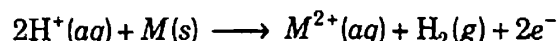


Fig. 16.3 Trends in electrode potentials of transition metals of 3d-series

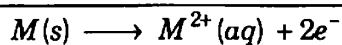
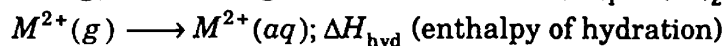
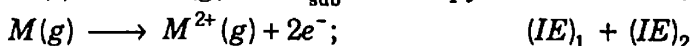
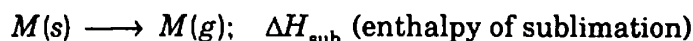
A qualitative treatment of the stability of transition metal ion in different oxidation states in aqueous medium is obtained from the electrode potential data. The value of  $E^\circ$  for  $M^{2+}/M$  denotes the emf of the cell in which the reaction



occurs under reversible conditions (values given in Table 16.1). The total energy  $\Delta H$  of process



can be represented as equal to sum of the energy of the following steps :



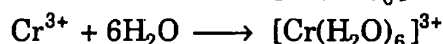
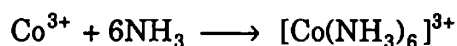
$$\Delta H = \Delta H_{\text{sub}} + (IE)_1 + (IE)_2 + \Delta H_{\text{hyd}}$$

### DEEP Focus

- Although the transition metals are less electropositive (or more electronegative) than the alkali and alkaline-earth metals, their standard reduction potentials suggest that all of them except copper should react with strong acids such as dil. HCl to produce  $H_2$  gas. However, most transition metals are inert towards acids or react slowly with them because of a protective layer of oxide. In case of Cr, despite a negative standard reduction potential, it is quite inert chemically because of the formation of chromium (III) oxide,  $Cr_2O_3$  on its surfaces. This fact find application of Cr to use as a protective and noncorrosive plating on other metals.

## Complexes

The transition elements have an unparalleled tendency to form coordination compounds with Lewis bases that is with groups which are able to donate an electron pair (called ligands). A ligand may be a neutral molecule such as  $NH_3$ , or an ion such as  $Cl^{-}$  or  $CN^{-}$ .



This ability to form complexes is in marked contrast to the *s*- and *p*-block elements which form only a few complexes. Tendency to form complexes by transition metal is due to :

- their smaller size,
- higher nuclear charge,
- presence of low energy vacant orbitals to accept lone pair of electrons donated by ligands.

Complexes where the metal is in the (III) oxidation states are generally more stable than those where the metal is in the (II) state. Thus,  $[Fe^{III}(CN)_6]^{3-}$  is more stable than  $[Fe^{II}(CN)_6]^{4-}$  (Detailed study of the complexes is given in Chapter 18 of the Text.

## Electronegativity

Transition elements have fairly low values of electronegativity. It increases from Sc to Cu with a fall at Mn and Zn. However, this increase in electronegativity is much slower because the additional electron is being

added to an inner shell which provides relatively good shielding to the outer electrons from the nucleus. The increasing electronegativity from Sc to Cu means that the elements become slightly less metallic and this is reflected in the increasing positive electrode potentials of their ions  $M^{2+}$  and  $M^{3+}$  (Table 16.1)

## Magnetic Properties

When you place an iron piece near a magnet, you will see that it is immediately drawn towards the magnet. However, some elements are repelled by the magnets. The property of an element to be attracted or repelled by a magnet differs from element to element. Substances which are weakly repelled by the magnetic field are called **diamagnetic** (with no unpaired electrons) while the substances which are weakly attracted by the magnetic field and lose their magnetism when removed from the field are called **paramagnetic**. If the force of attraction is very large and the permanent magnetisation is retained, the substance is said to be **ferromagnetic**, e.g., iron and some iron compounds.

The magnetic properties of any individual atom or ion will result from the combination of the two properties,

- inherent spin moment of the electron and
- the orbital moment resulting from the motion of the electron around the nucleus.

The magnetic moment is usually expressed in units called **Bohr magnetons** (BM). The general equation for the magnetic moment is given by :

$$\mu_{(S+L)} = \sqrt{4S(S+1) + L(L+1)}$$

In above expression, *S* is the sum of the spin quantum numbers and *L* is the sum of orbital angular momentum quantum numbers of all the electrons. In many compounds including those of the first row transition elements, the orbital contribution is compensated by the electric fields of the surrounding atoms and as an approximation, the observed magnetic moment may be considered to arise **only from unpaired spins**. Putting *L* = 0 in the above expression, you can get the spin-only magnetic moment  $\mu_S$ .

$$\text{Thus,} \quad \mu_S = \sqrt{4S(S+1)}$$

The spin-only magnetic moment,  $\mu_S$  can also be related to the number of unpaired electrons, *N*, in any species, as the total spin quantum number  $S = \frac{N}{2}$

$$\begin{aligned} \text{Hence,} \quad \mu_S &= \sqrt{4S(S+1)} \\ &= \sqrt{\frac{4N}{2} \left( \frac{N}{2} + 1 \right)} \\ \mu_S &= \sqrt{N(N+2)} \end{aligned}$$

Above expression gives the values of magnetic moment in Bohr magnetons which can be converted into SI unit of Ampere square meter ( $\text{A m}^2$ ) by the following relationship :

$$1 \text{ BM} = 9.274 \times 10^{-24} \text{ A m}^2$$

Magnetic moment increases as number of unpaired electrons increases. For 3d-series elements, variation of magnetic moment is given in Fig. 16.4. This clearly shows magnetic moment is maximum for chromium (with six unpaired electrons).

|       | Sc         | Ti         | V           | Cr          | Mn          | Fe          | Co          | Ni         | Cu         | Zn |
|-------|------------|------------|-------------|-------------|-------------|-------------|-------------|------------|------------|----|
| Z     | 21         | 22         | 23          | 24          | 25          | 26          | 27          | 28         | 29         | 30 |
| N     | 1          | 2          | 3           | 6           | 5           | 4           | 3           | 2          | 1          | 0  |
| $\mu$ | $\sqrt{3}$ | $\sqrt{8}$ | $\sqrt{15}$ | $\sqrt{48}$ | $\sqrt{35}$ | $\sqrt{24}$ | $\sqrt{15}$ | $\sqrt{8}$ | $\sqrt{3}$ | 0  |

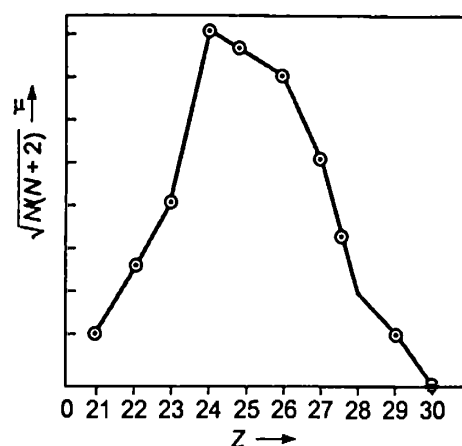


Fig. 16.4 Magnetic moment of 3d-series elements (on arbitrary scale)

In some cases (e.g.,  $\text{Mn}^{2+}$ , or  $\text{Fe}^{3+}$ , in which all the d-orbitals are occupied singly by electrons for which  $m_l = 2, 1, 0, -1$  and  $-2$ , giving  $L = 0$ ) the observed magnetic moment values agree very well with the spin-only value as given in Table 16.3. But generally, experimental values differ from the spin-only values. This is because the orbital motion of the electron also makes some contribution to the moment.

Table 16.3 Predicted and Observed Magnetic Moment Values of Some Transition Metal Hydrated Ions

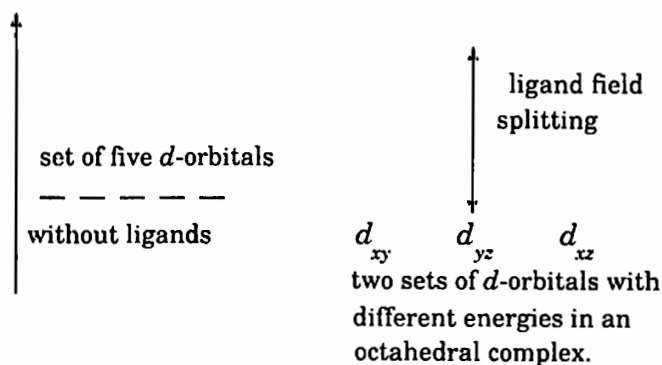
| Ion                                      | Electronic configuration                                                                        | Unpaired electrons | Magnetic moment (BM) |                            |
|------------------------------------------|-------------------------------------------------------------------------------------------------|--------------------|----------------------|----------------------------|
|                                          |                                                                                                 |                    | [Calculated]         | [Experimental ( $\mu_s$ )] |
| $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ | $3d^1 \uparrow$                                                                                 | 1                  | 1.73                 | 1.75                       |
| $[\text{V}(\text{H}_2\text{O})_6]^{3+}$  | $3d^2 \uparrow \uparrow$                                                                        | 2                  | 2.84                 | 2.75                       |
| $[\text{V}(\text{H}_2\text{O})_6]^{2+}$  | $3d^3 \uparrow \uparrow \uparrow$                                                               | 3                  | 3.87                 | 3.86                       |
| $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ | $3d^4 \uparrow \uparrow \uparrow \uparrow$                                                      | 4                  | 4.90                 | 4.80                       |
| $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ | $3d^5 \uparrow \uparrow \uparrow \uparrow \uparrow$                                             | 5                  | 5.92                 | 5.96                       |
| $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ | $3d^6 \uparrow \downarrow \uparrow \uparrow \uparrow \downarrow$                                | 6                  | 4.90                 | 5.00                       |
| $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ | $3d^7 \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow$                       | 7                  | 3.87                 | 4.40                       |
| $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ | $3d^8 \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow$            | 8                  | 2.84                 | 2.90                       |
| $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ | $3d^9 \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow$ | 9                  | 1.73                 | 1.80                       |

## Colour

Many ionic and covalent compounds of transition elements (and also inner transition elements) are coloured. In contrast, compounds of the s- and p- block elements are almost always white. Colour may arise from an entirely different cause in ions with incomplete d or f-shells. In a free isolated gaseous ions, the five d-orbitals are degenerate, that is, they are identical in energy. The surrounding groups, which can be solvent molecules in solution or ligands in a complex or other ions in a crystal lattice, affect the energy of some d-orbitals more than others. Thus, the d-orbitals no longer degenerate and at their simplest they form two groups of orbitals of different energy. Thus in transition element with a partly filled d- shell, it is possible to promote electrons from one

d-level to another  $d^*$  level of higher energy (called d-d\* transition). This corresponds to a fairly small energy difference, and so light is absorbed in the visible region. The colour of a transition metal complex is dependent on how big the energy difference is between the two d-levels. This in turn depends on the nature of the ligand, and the type of the complex formed. The colour which we see is the colour of the transmitted wavelength and is the complimentary colour absorbed by the compounds

|                                          |                       |
|------------------------------------------|-----------------------|
| $[\text{Ni}(\text{NH}_3)_6]^{2+}$        | blue                  |
| $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ | green                 |
| $[\text{Ni}(\text{NO}_2)_6]^{2-}$        | brown-red             |
| Energy                                   | $d_z^2$ $d_{x^2-y^2}$ |



- $\text{ZnSO}_4$  ( $\text{Zn}^{2+}$  with  $d^{10}$  configuration) and  $\text{TiO}_2$  ( $\text{Ti}^{4+}$  with  $d^0$ -configuration) are white—in both of them  $d-d^*$  spectra are impossible and they are colourless.

### DEEP Focus

- In the series Sc (+III), Ti (+IV), V (+V) Cr (+VI) and Mn (+VII), all have empty  $d$ -orbitals, hence  $d-d^*$  spectra are impossible and they should be colourless. But following ions in aqueous solution are:

|                     |                        |                  |
|---------------------|------------------------|------------------|
| $\text{VO}_2^{2+}$  | (oxidation state +V)   | — pale yellow    |
| $\text{CrO}_4^{2-}$ | (oxidation state +VI)  | — deep yellow    |
| $\text{MnO}_4^-$    | (oxidation state +VII) | — intense purple |

The colours arise by charge transfer, for example, in  $\text{MnO}_4^-$  an electron is momentarily transferred from O to the metal and thus oxygen changes from  $\text{O}^{2-}$  to  $\text{O}^-$  and manganese from Mn(+VII) to Mn(+VI). (Also refer Chapter 18 of this Text). Table 16.4 gives the colour and oxidation states of the metal ions present in some hydrated ions of transition elements.

Table 16.4 Oxidation States and Observed Colours for Some Aqua Species

| Element | +2                                                     | +3                                                        | +6                                                                  | +7                         |
|---------|--------------------------------------------------------|-----------------------------------------------------------|---------------------------------------------------------------------|----------------------------|
| Sc      |                                                        | Colourless<br>$[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$    |                                                                     |                            |
| Ti      |                                                        | Violet<br>$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$        |                                                                     |                            |
| V       | Violet<br>$[\text{V}(\text{H}_2\text{O})_6]^{2+}$      | Green<br>$[\text{V}(\text{H}_2\text{O})_6]^{3+}$          |                                                                     |                            |
| Cr      | Blue<br>$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$       | Violet/green<br>$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  | Orange yellow<br>$\text{Cr}_2\text{O}_7^{2-}$ , $\text{CrO}_4^{2-}$ |                            |
| Mn      | Pink<br>$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$       | Red<br>$[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$           | Green<br>$\text{MnO}_4^{2-}$                                        | Purple<br>$\text{MnO}_4^-$ |
| Fe      | Pale green<br>$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ | Yellow/ brown<br>$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ |                                                                     |                            |
| Co      | Pink<br>$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$       | Blue<br>$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$          |                                                                     |                            |
| Ni      | Green<br>$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$      |                                                           |                                                                     |                            |
| Cu      | Blue<br>$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$       |                                                           |                                                                     |                            |
| Zn      | Colourless<br>$[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ |                                                           |                                                                     |                            |

## Size of Atoms and Ions

- The covalent radii of the elements (summarised in Table 16.5) decrease from left to right across a row in the transition series, until near the end when the size increases slightly. On passing from left to right, extra protons are placed in the nucleus and extra orbital electrons are added. The orbital electrons shield the nucleus charge incompletely (order being  $d < p < s$ ). Thus the nuclear charge attracts all the electrons more strongly, hence, a contraction in size occurs.

### DEEP Focus

- The radii of the elements from chromium to copper, however, are very close to one another. This is due to the fact that successive addition of  $d$ -electrons screen the outer electrons ( $4s$ ) from the inward pull of the nucleus. As a result of this, the size of the atom does not alter much in moving from chromium to copper.
- The relative constancy in covalent radii for the later elements is partly responsible for the similarity in properties of the Groups 8, 9 and 10 (VIII B) elements (which are Fe, Co, and Ni).
- Atoms of the transition elements are smaller than those of the Group I or II elements ( $s$ -block) in the same horizontal period. This is partly because of the usual contraction in size across a horizontal period and partly because the orbital electrons are added to the penultimate  $d$ -shell rather than to the outer shell of the atom.

However, it is important to emphasise here that shielding of the outer  $ns$ -electron(s) by  $(n-1)$   $d$ -electron(s) is more efficient than the shielding of a  $ns$ -electron by another  $ns$  electron (or that of a  $np$ -electron by another  $np$ -electron). This is why the decrease in atomic radius from sodium to chlorine is greater than that from scandium to copper. The elements which occur immediately after the transition elements are smaller than expected from simple.

The rate of decrease in size along the lanthanide series is even less than that in the transition series since in the lanthanides the electrons are added to the penultimate  $[(n-2)f]$  shell and these shield the outer electrons much more effectively. The presence of  $4f$ -electrons in the lanthanides affects the atomic size and therefore, the chemistry of the elements following the lanthanides. The atomic radii of the elements of third transition series are much smaller than expected. This is due to the effect of the greater than expected effective nuclear charge felt by the electrons of the elements of the third row transition series, hafnium to gold, owing to the insertion of lanthanides.

### Metallic radii (pm) of some elements of Group 1-13

| 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  | 13  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| K   | Ca  | Sc  | Ti  | V   | Cr  | Mn  | Fe  | Co  | Ni  | Cu  | Zn  | Ga  |
| 235 | 197 | 164 | 147 | 135 | 130 | 135 | 126 | 125 | 125 | 128 | 137 | 141 |
| Rb  | Sr  | Y   | Zr  | Nb  | Mo  | Tc  | Ru  | Rh  | Pd  | Ag  | Cd  | In  |
| 248 | 215 | 178 | 160 | 146 | 139 | 136 | 134 | 134 | 137 | 144 | 154 | 166 |
| Cs  | Ba  | La  | Hf  | Ta  | W   | Re  | Os  | Ir  | Pt  | Au  | Hg  | Tl  |
| 267 | 222 | 188 | 160 | 149 | 141 | 137 | 135 | 136 | 139 | 146 | 157 | 171 |



Data in Table 16.1 and Fig. 16.5 show that the general trend of decreasing size is reversed towards the end of the series. This could be due to an increase in inter-electronic repulsion after the addition of sufficient number of electrons in the *d*-orbitals leading to the gradual increase in size.

Table 16.5 Covalent Radii of the Transition Elements (pm)

| K   | Ca  | Sc  | Ti  | V   | Cr  | Mn  | Fe  | Co  | Ni  | Cu  | Zn  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 203 | 174 | 144 | 132 | 122 | 117 | 117 | 117 | 116 | 115 | 117 | 125 |
|     |     |     | Zr  | Nb  |     |     |     |     |     |     |     |
|     |     |     | 145 | 134 |     |     |     |     |     |     |     |
|     |     |     | Hf  | Ta  |     |     |     |     |     |     |     |
|     |     |     | 144 | 134 |     |     |     |     |     |     |     |

There is a gradual decrease in size of the 14 lanthanide elements from cerium (58) to lutetium (71). This is called **Lanthanide Contraction**. *The lanthanide contraction cancels almost exactly the normal size increase on descending a group of transition elements. Thus covalent and ionic radii of Nb are the same as the values for Ta. Same is the case for Zr and Hf (also refer Table 16.6 and Fig. 16.5).*

Table 16.6 Effect of Lanthanide Contraction on Ionic Radii (pm)

|                      |                        |                       |                       |
|----------------------|------------------------|-----------------------|-----------------------|
| Ca <sup>2+</sup> 100 | Sc <sup>3+</sup> 74.5  | Ti <sup>4+</sup> 60.5 | V <sup>3+</sup> 64.0  |
| Sr <sup>2+</sup> 118 | Y <sup>3+</sup> 90.0   | Zr <sup>4+</sup> 72.0 | Nb <sup>3+</sup> 72.0 |
| Ba <sup>2+</sup> 135 | La <sup>3+</sup> 103.2 | Hf <sup>4+</sup> 71.0 | Ta <sup>3+</sup> 72.0 |

*The effects of lanthanide contraction are less pronounced towards the right of the d-block.*

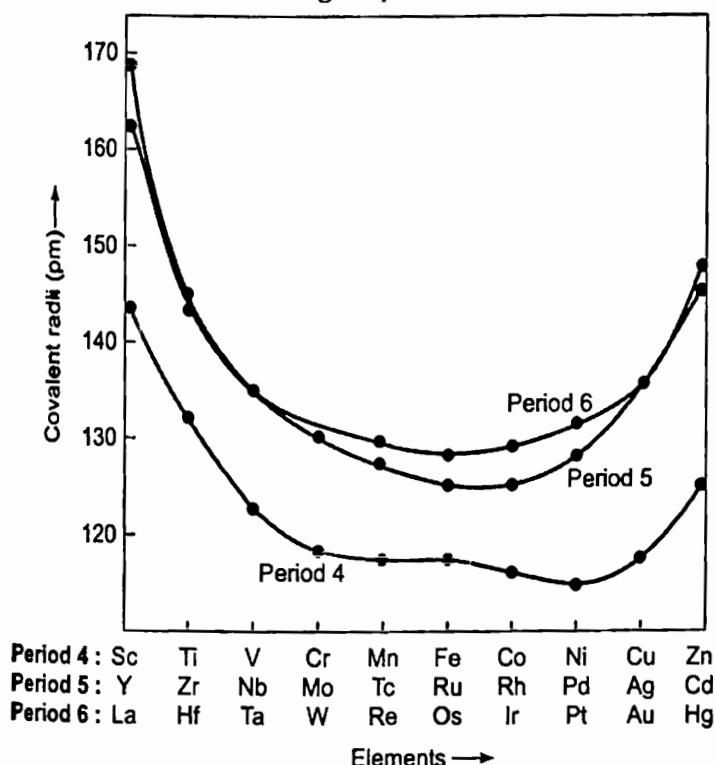


Fig. 16.5 Comparison of the covalent radii for transition elements of different periods. Note that elements in the same column of the fifth and sixth periods have approximately the same radii.

Atomic volume of an element is directly related to its size and therefore, atomic volumes follow the same trend as the atomic size. Similarly density is also related to the size of the element. The smaller the size, the higher the density of the element as shown in Fig. 16.6. For 4*d* and 5*d* elements, this increase is not as regular as the increase in densities for 3*d*-elements.

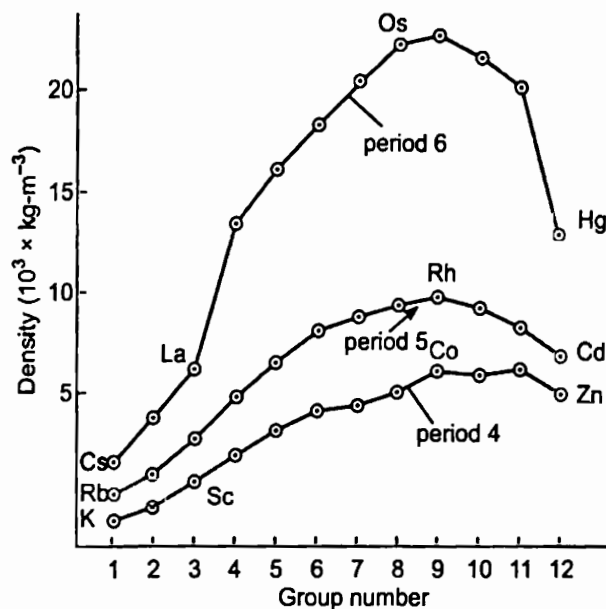
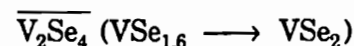
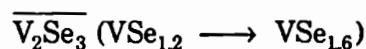
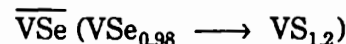


Fig. 16.6 Trend in densities of the alkali, alkaline earth and transition metals of the fourth, fifth and sixth periods.

## Non-stoichiometry

Transition elements have the property of forming compounds of indefinite structures and proportions. These are called **Non-stoichiometric** compounds. **Iron (II) oxide FeO is written as  $\overline{\text{FeO}}$  to indicate that ratio of Fe and O atoms is not exactly 1 : 1.** Analysis shows that the formula varies between  $\text{Fe}_{0.94}\text{O}$  and  $\text{Fe}_{0.84}\text{O}$ . Vanadium and selenium form a series of compounds ranging from  $\text{VSe}_{0.98}$  to  $\text{VSe}_2$  :



$\text{CuS}$  (insoluble) is actually a mixture of  $\text{CuS}$  and  $\text{Cu}_2\text{S}$ . Non-stoichiometry is shown particularly among transition metal compounds of the Group VI elements (O, S, Se, Te) and is mostly due to **variable valency** of transition elements, and also sometimes due to **defects** in solid structures.

## Catalytic Properties

Many transition metals and their compounds have catalytic properties.



### DEEP Focus

These metals can function as catalysts because they can utilise both *d* and *s*-electrons for the formation of bonds between reactant molecules and the surface catalyst atoms. This increases the concentration of the reactants at the catalyst surface and weakens the bonds in the reactant molecules with the result that the activation energy is lowered. Compounds of transition metals are able to act as catalysts because of the ease with which the metal can adopt different oxidation states and also because of their ability to form complexes.

Some of the common catalysts used for important reactions are summarised in Table 16.7.

Table 16.7 Transition Metals and their Compounds as Catalyst

| Catalyst                                          | Function                                                                                                                                                                                                                             |
|---------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| TiCl <sub>4</sub>                                 | Used as Ziegler Natta catalyst in the production of polythene                                                                                                                                                                        |
| FeSO <sub>4</sub> + H <sub>2</sub> O <sub>2</sub> | Used as Fenton's reagent in the oxidation of alcohols to aldehydes.                                                                                                                                                                  |
| Ni                                                | Raney nickel in reduction processes :<br>—manufacture of hexamethylenediamine,<br>—production of H <sub>2</sub> from NH <sub>3</sub> ,<br>—reducing anthraquinone to anthraquinol in the production of H <sub>2</sub> O <sub>2</sub> |
| Ni complexes                                      | Reppe synthesis (polymerisation of alkynes to give benzene, cyclooctatetraene).                                                                                                                                                      |
| Cu                                                | Used in manufacturing of (CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub> being used to make silicones.                                                                                                                             |
| Cu/V                                              | Used in the oxidation of cyclohexanol/cyclohexanone mixture to acetic acid which is used to prepare Nylon-66.                                                                                                                        |
| CuCl <sub>2</sub>                                 | Deacon process of making Cl <sub>2</sub> from HCl.                                                                                                                                                                                   |
| MnO <sub>2</sub>                                  | Used in the decomposition of KClO <sub>3</sub> to KCl and O <sub>2</sub> .                                                                                                                                                           |
| V <sub>2</sub> O <sub>5</sub>                     | Used in contact process of H <sub>2</sub> SO <sub>4</sub> .                                                                                                                                                                          |
| Fe/Mo                                             | Promoted Fe used in the Haber-Bosch process of NH <sub>3</sub>                                                                                                                                                                       |
| FeCl <sub>3</sub>                                 | Used in the production of CCl <sub>4</sub> from CS <sub>2</sub> and Cl <sub>2</sub>                                                                                                                                                  |
| PdCl <sub>2</sub>                                 | Wacker process for converting C <sub>2</sub> H <sub>4</sub> into CH <sub>3</sub> CHO.                                                                                                                                                |
| Pt/PtO                                            | Adams catalyst in reduction.                                                                                                                                                                                                         |
| Pt                                                | In three stage convertors for cleaning car exhaust fumes.                                                                                                                                                                            |
| Pt/Rh                                             | In Ostwald process for HNO <sub>3</sub> from NH <sub>3</sub>                                                                                                                                                                         |
| ZnO/CuO                                           | In synthesis of CH <sub>3</sub> OH from CO and H <sub>2</sub>                                                                                                                                                                        |
| Co/Fe                                             | In synthesis of hydrocarbons by CO and H <sub>2</sub> in Fischer-Tropsch process.                                                                                                                                                    |
| Pt/PtO                                            | Adians Catalyst for reduction                                                                                                                                                                                                        |

Enzymes are catalysts that enhance the rates of specific reactions. Some enzymes require the presence of metal ions as cofactors called as **metalloenzymes** which generally contain transition metal, *e.g.*, Mo in xanthine oxidase (metabolism of purines).

A cobalt atom lies at the centre of the vitamin B<sub>12</sub> coenzyme. Iron atoms are importantly involved in haemoglobin of blood and in the ferredoxins of photosynthetic process. Fe and Mo are present in nitrogen fixing enzyme.

### Alloy Formation

An alloy is a blend of metals prepared by mixing the components. Alloys (refer Appendix VI) may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15 per cent of each other. Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys so formed are hard and have often high melting points. The best known are ferrous alloys; chromium, vanadium, tungsten, molybdenum, and manganese are used for the production of variety of steels and stainless steel. Alloys of transition metals with non-transition metals as brass (copper-zinc), and bronze (copper-tin) are also of considerable industrial importance.

### Interstitial Compounds

- Transition metals can trap some small atoms like hydrogen, boron carbon, nitrogen, etc., in vacant spaces in their crystal lattice forming interstitial compounds. Carbon and nitrogen always occupy octahedral holes; hydrogen is smaller and always occupies tetrahedral holes. As only transition metals form such compounds, the *d*-electrons are, therefore, presumably involved in the bonding. The structure of the metal often changes during the formation of such compounds. The composition of these compounds is generally non-stoichiometric, *e.g.*, TiH<sub>1.73</sub>, PdH<sub>0.56</sub>, VH<sub>0.56</sub>, but may approach regular stoichiometry and a regular structure, *e.g.*, TiC and VN. The later transition elements of the first series form non-stoichiometric carbides with irregular structures, such as Cr<sub>7</sub>C<sub>3</sub>, which are more reactive than the interstitial carbides of the early transition elements. These interstitial compounds are of much importance, *e.g.*, carbon steels are interstitial iron-carbon compounds in which the interstitial carbon prevents the iron atoms from sliding over one another, making iron harder, stronger but more brittle.

### Nature of Oxides/Hydroxides

While moving along a period from Sc to Zn basic nature decreases and acidic nature increases. Behaviour differs when oxidation states are different

|                                |                  |                               |                                |                  |                                |                                |     |     |     |
|--------------------------------|------------------|-------------------------------|--------------------------------|------------------|--------------------------------|--------------------------------|-----|-----|-----|
| Sc <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | V <sub>2</sub> O <sub>5</sub> | Cr <sub>2</sub> O <sub>3</sub> | MnO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | Co <sub>2</sub> O <sub>3</sub> | NiO | CuO | ZnO |
| A                              | A                | A                             | A                              | A                | B                              | B                              | B   | B   | A   |

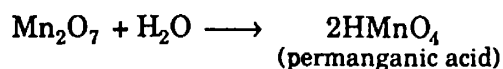
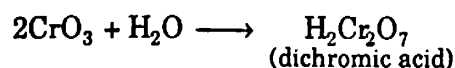
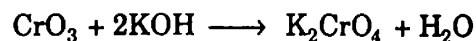
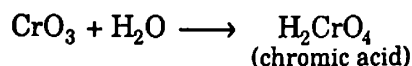
A : Amphoteric, B : Basic

With increase in the oxidation state of a given transition metal, the covalent character of its compound increases and thus acidic character also increases.

|                       | MnO   | Mn <sub>3</sub> O <sub>4</sub> | Mn <sub>2</sub> O <sub>3</sub> | MnO <sub>2</sub> | MnO <sub>3</sub> | Mn <sub>2</sub> O <sub>7</sub> |
|-----------------------|-------|--------------------------------|--------------------------------|------------------|------------------|--------------------------------|
| Oxidation state of Mn | +2    | +8/3                           | +3                             | +4               | +6               | +7                             |
| Nature of oxide       | Basic | Amphoteric                     |                                |                  | Weakly acidic    | Strongly acidic                |

Characteristics of oxides and ions of vanadium and chromium have been summarised in Table 16.8.

The basic and amphoteric oxides dissolve in non-oxidising acids and form hexaaquo ions  $[M(H_2O)_6]^{n+}$ . The acidic oxides like  $CrO_3$  and  $Mn_2O_7$  dissolve in water to form the oxyacids. These oxides also react with bases to form oxosalts.



As we move along a given transition series, +2 oxidation state of the metals becomes more and more stable and hence the tendency of these metals to lose electrons increases hence, reducing nature of the metal oxide increases. VO and CrO are strong reducing agents.

Table 16.8 Characteristics of Oxides and Some Ions of V and Cr

| O.S. | Oxide/ Hydroxide                               | Behaviour  | Ion                            | Name of ion                                           | Colour of ion        |
|------|------------------------------------------------|------------|--------------------------------|-------------------------------------------------------|----------------------|
| +2   | VO                                             | basic      | $V^{2+}$                       | vanadium (II) (vanadous)                              | violet               |
| +3   | $V_2O_5$                                       | basic      | $V^{3+}$                       | vanadium (III) (vanadic)                              | green                |
| +4   | $VO_2$                                         | amphoteric | $VO^{2+}$                      | oxovanadium (IV) (vanadyl)<br>hypovanadate (vanadite) | blue                 |
|      |                                                |            | $V_4O_{10}^{2-}$               |                                                       | brown                |
| +5   | $V_2O_5$                                       | amphoteric | $VO_2^+$<br>$VO_4^{3-}$        | dioxovanadium (V) orthovanadate                       | yellow<br>colourless |
| +2   | $CrO$ ]<br>$Cr(OH)_2$ ]                        | basic      | $Cr^{2+}$                      | chromium (II) (chromous)                              | light blue           |
| +3   | $Cr_2O_3$ ]<br>$Cr(OH)_3$ ]                    | amphoteric | $Cr^{3+}$<br>$[Cr(OH)_4]^-$    | chromium (III) (chromic)<br>chromite                  | violet<br>green      |
| +6   | $CrO_3$ ]<br>$CrO_2(OH)_2$ ]<br>$H_2Cr_2O_7$ ] | acidic     | $CrO_4^{2-}$<br>$Cr_2O_7^{2-}$ | chromate<br>dichromate                                | yellow<br>orange     |

Table 16.9 Fourth Period Transition Elements Essential to Human Nutrition

| Element   | Some biochemical substances                                                          | Functions                                                                                |
|-----------|--------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| Chromium  | Glucose tolerance factor                                                             | Utilisation of glucose                                                                   |
| Cobalt    | Cobalamin (vitamin B <sub>12</sub> )                                                 | Development of red blood cells                                                           |
| Copper    | Ceruloplasmin<br>Cytochrome oxidase                                                  | Synthesis of haemoglobin<br>Cell energetics                                              |
| Iron      | Haemoglobin and myoglobin<br>Cytochrome C<br>Catalase                                | Transport and storage of oxygen<br>Cell energetics<br>Decomposition of hydrogen peroxide |
| Manganese | Isocitrate dehydrogenase                                                             | Cell energetics                                                                          |
| Zinc      | Carbonic anhydrase<br>Carboxypeptidase A (Pancreatic juice)<br>Alcohol dehydrogenase | Elimination of CO <sub>2</sub><br>Protein digestion<br>Oxidation of ethanol              |

## Target Practice 1

- What are the types of the following reactions?  
 (a)  $3\text{CrO}_4^{2-} + 8\text{H}^+ \longrightarrow 2\text{CrO}_4^{2-} + \text{Cr}^{3+} + 4\text{H}_2\text{O}$   
 .....  
 (b)  $3\text{MnO}_4^{2-} + 4\text{H}^+ \longrightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$   
 .....
- Write EC of  
 (a) Cu(II) .....  
 (b) Cr(0) .....  
 (c) Co(III) .....
- Name the element with maximum oxidation state in *d*-block elements  
 .....
- (a)  $\text{Cr}^{2+}$  is unstable in .....  
 (b)  $\text{Fe}^{2+}$  is oxidised to  $\text{Fe}^{3+}$  in .....
- Why a transition series contains ten elements?  
 .....  
 .....
- (*IE*)<sub>1</sub> of 5*d*-elements are higher than those of the 3*d* and 4*d* elements. It is due to .....
- Stepwise (*IE*)<sub>s</sub> of Ni and Pt are given below
 

|    | ( <i>IE</i> ) <sub>1</sub> + ( <i>IE</i> ) <sub>2</sub> | ( <i>IE</i> ) <sub>3</sub> + ( <i>IE</i> ) <sub>4</sub> |
|----|---------------------------------------------------------|---------------------------------------------------------|
| Ni | 2.49                                                    | 8.80                                                    |
| Pt | 2.66                                                    | 6.70                                                    |

Compare thermodynamic stability of Ni and Pt salts in (II) and (IV) oxidation state  
 Ni(II) ☐ Pt(II)  
 Ni(IV) ☐ Pt(IV)
- E*<sup>o</sup> values of reactions
 
$$\text{Fe}^{2+} + 2\text{e}^- \longrightarrow \text{Fe}; \quad E^\circ = -0.44 \text{ V}$$

$$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}; \quad E^\circ = +0.34 \text{ V}$$

The *E*<sup>o</sup> of  $\text{Fe} + \text{Cu}^{2+} \rightleftharpoons \text{Fe}^{2+} + \text{Cu}$  is ..... and thus, reaction is spontaneous/non-spontaneous.
- Select ions which can form complexes out of  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$   
 .....  
 .....
- Which complex is more stable in each pair?  
 (a)  $[\text{Fe}(\text{CN})_6]^{4-}$  ☐  $[\text{Fe}(\text{CN})_6]^{3-}$   
 (b)  $[\text{Ni}(\text{CN})_4]^{2-}$  ☐  $[\text{Pt}(\text{CN})_4]^{2-}$   
 (c)  $[\text{NiCl}_6]^{2-}$  ☐  $[\text{PtCl}_6]^{2-}$
- Mention three factors which favour formation of complexes by *d*-block elements  
 (a) .....  
 (b) .....  
 (c) .....
- State whether the following complexes are coloured or not  
 (a)  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  Yes/No  
 (b)  $[\text{Cu}(\text{CN})_4]^{3-}$  Yes/No  
 (c)  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  Yes/No  
 (d)  $[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$  Yes/No
- Consider following complexes  
 I :  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  II :  $[\text{Fe}(\text{CN})_6]^{4-}$   
 III :  $[\text{Ni}(\text{CO})_4]$  IV :  $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$   
 V :  $[\text{Ni}(\text{CN})_4]^{2-}$   
 Out of these select the complex(es) with.  
 (a) Maximum number of unpaired electrons .....  
 (b) Maximum number of magnetic moment .....  
 (c) Equal number of unpaired electrons .....  
 (d) Equal magnetic moment .....  
 (e) Square planar geometry .....  
 (f) Octahedral geometry .....  
 (g) Tetrahedral geometry .....
- Convert 3.00 BM into SI unit ( $\text{A m}^2$ )  
 .....
- Calculate magnetic moment of  $\text{V}^{3+}$  (*Z* = 23)  
 ..... BM
- What is oxidation state of iron in  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ ?  
 .....
- Give one example in which ion is coloured due to charge transfer.  
 .....  
 .....
- Give oxidation of the underlined and give the colour of the ion
 

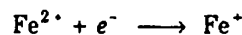
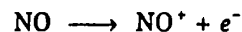
|                     | Oxidation state | Coloured/colourless |
|---------------------|-----------------|---------------------|
| $\text{VO}_2^+$     | .....           | .....               |
| $\text{CrO}_4^{2-}$ | .....           | .....               |
- Give examples of coloured ions with following oxidation state  
 (a) Cr(VI) .....  
 (b) Cu (II) .....  
 (c) Mn(VI) .....  
 (d) Ni(II) .....  
 (e) V(III) .....  
 (f) Co(III) .....

## Answers

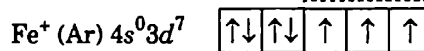
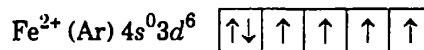
- (a)  $\text{CrO}_4^{2-}$  (V) is oxidised to  $\text{CrO}_4^{2-}$  (VI) and reduced to  $\text{Cr}^{3+}$  (III)  
 (b)  $\text{MnO}_4^{2-}$  (VI) is oxidised to  $\text{MnO}_4^-$  (VII) and reduced to  $\text{MnO}_2$  (IV)  
 Thus, (a) and (b) both disproportionation reactions.
- (a)  $[\text{Ar}] 3d^9$  (b)  $[\text{Ar}] 3d^5 4s^1$  (c)  $[\text{Ar}] 3d^6$
- Os, Ru(VIII)
- (a) water (b) aerated water ( $\text{CO}_2$  mixed water)
- In transition series, the electrons enter the *d*-orbitals which can accommodate ten electrons and therefore, there are ten elements in one transition series.
- This is due to greater effective nuclear charge acting on outer valence electrons because of the weak shielding of the nucleus by 4*f*-electrons.

7.  $\text{Ni(II)} > \text{Pt(II)}$   
 $\text{Ni(IV)} < \text{Pt(IV)}$
8.  $E^\circ = E^\circ_{\text{Fe}^{2+}/\text{Fe}} + E^\circ_{\text{Cu}^{2+}/\text{Cu}}$   
 $= -(-0.44) + 0.34 = 0.78 \text{ V}$   
 Spontaneous.
9.  $\text{Fe}^{2+}, \text{Ni}^{2+}, \text{Ca}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Mg}^{2+}$   
 $(\text{Ca}^{2+} \text{ and } \text{Mg}^{2+} \text{ form complexes with EDTA})$
10. (a)  $[\text{Fe}(\text{CN})_6]^{4-} < [\text{Fe}(\text{CN})_6]^{3-}$   
 (b)  $[\text{Ni}(\text{CN})_4]^{2-} > [\text{Pt}(\text{CN})_4]^{2-}$   
 (c)  $[\text{NiCl}_6]^{2-} < [\text{PtCl}_6]^{2-}$
11. (a) Smaller size,  
 (b) Higher nuclear charge,  
 (c) Presence of low energy vacant orbitals to accept lone pair of electrons donated by ligands.
12. (a) No (b) No (c) Yes (d) No  
 (Complex with unpaired electrons in  $d$ -orbital in the atom/ion is coloured)
13. (a) I (b) I (c) None (d) None  
 (e) V (f) I, II (g) III, IV
14.  $3 \times 9.274 \times 10^{-24} \text{ A m}^2$
15.  $V(Z = 23) : [\text{Ar}] 4s^2 3d^3$   
 $V^{3+} : [\text{Ar}] 4s^0 3d^2$   
 Magnetic moment =  $\sqrt{N(N+2)} \text{ BM} = \sqrt{8} \text{ BM}$
16. This is a typical case of complex formed by electron exchange.

NO change to  $\text{NO}^+$  by loss of electron and this electron is gained by  $\text{Fe}^{2+}$  which change to  $\text{Fe}^+$



Thus, oxidation state of iron = + 1

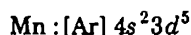


Three unpaired electrons

+1 oxidation state is confirmed by magnetic moment of iron  
 $= \sqrt{15} = 3.87 \text{ BM}$  and also by diamagnetic character of  $\text{NO}$ .  
 (which is only possible when it has no unpaired electron)

#### 17. $\text{MnO}_4^-$

Mn is in +7 oxidation state,



$\text{Mn}^{2+} : [\text{Ar}]$  with no unpaired electrons; oxygen atom transfers electrons to Mn (in its  $d$ -orbital) and thus  $\text{MnO}_4^-$  is coloured.

#### Oxidation state

18.  $\text{VO}_2^+$  +5 coloured  
 $\text{CrO}_4^{2-}$  +6 coloured
19. (a)  $\text{CrO}_4^{2-}$  (b)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  (c)  $\text{MnO}_4^{2-}$   
 (d)  $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$  (e)  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$  (f)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$

## Practice Exercise 1

1. What is the oxidation state of the underlined atoms in  
 (a)  $\underline{\text{Ni}}(\text{CO})_4$  (b)  $\text{MnO}_4^{2-}$   
 (c)  $\underline{\text{Cr}}\text{O}_2\text{Cl}_2$  (d)  $\underline{\text{Cr}}\text{O}_5$   
 (e)  $[\underline{\text{Cr}}(\text{CN})_6]^{3-}$  (f)  $[\underline{\text{Fe}}(\text{CN})_5\text{NO}]^{2-}$
2. Give the electron configuration of the metal in each of the following atoms or ions:  
 (a) Ni (b)  $\text{Cr}^{3+}$   
 (c)  $\text{FeO}_4^{2-}$  (ferrate ion) (d)  $\text{MnO}_2$
3. Arrange the following hydroxy compounds in order of increasing acid strength, and account for the trend  
 (a)  $\text{CrO}_2(\text{OH})_2$  (b)  $\text{Cr}(\text{OH})_2$   
 (c)  $\text{Cr}(\text{OH})_3$
4. Explain how  $\text{Cr}(\text{OH})_3$  can act both as an acid and as a base.
5.  $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$ ,  $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$ ,  $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V}$   
 Calculate  $E^\circ$  values of following reactions :  
 (a)  $2\text{Ag}^+ + \text{Cu} \longrightarrow 2\text{Ag} + \text{Cu}^{2+}$   
 (b)  $\text{Cu} + \text{Zn}^{2+} \longrightarrow \text{Zn} + \text{Cu}^{2+}$   
 (c)  $2\text{Ag} + \text{Zn}^{2+} \longrightarrow 2\text{Ag}^+ + \text{Zn}$   
 Are they spontaneous.
6. Following arbitrary values are given for the conversion of  $M(s)$  into  $M^{2+}(aq)$   
 $M(s) \longrightarrow M(g); \quad \Delta H = 1000 \text{ kJ mol}^{-1}$   
 $M(g) \longrightarrow M(g) + e^-; \quad \Delta H = 950 \text{ kJ mol}^{-1}$   
 $M^+(g) \longrightarrow M^{2+}(g) + e^-; \quad \Delta H = 1100 \text{ kJ mol}^{-1}$   
 $M^{2+}(g) + aq \longrightarrow M^{2+}(aq); \quad \Delta H = -750 \text{ kJ mol}^{-1}$   
 Calculate  $\Delta H$  for  
 $M(s) \longrightarrow M^{2+}(aq) + 2e^-$

7. Which of the following compounds in each pair is more stable?  
 (a)  $\text{K}_2[\text{PtCl}_6]$   $\text{K}_2[\text{NiCl}_6]$   
 (b)  $[\text{Ni}(\text{CN})_4]^{2-}$   $[\text{Pt}(\text{CN})_4]^{2-}$   
 (c)  $\text{PtCl}_4$   $\text{NiCl}_4$   
 (d)  $\text{PtCl}_2$   $\text{NiCl}_2$
8. Why does chromium seem to be less reactive than its standard reduction potential suggests?
9. Write a balanced net ionic equation for reaction of each of the following metals with HCl in the absence of air. If no reaction occurs, indicate N.R.  
 (a) Cr (b) Zn  
 (c) Cu (d) Fe
10.  $[\text{Fe}^{III}(\text{CN})_6]^{3-}$  ion has magnetic moment of 1.73 B.M., while  $[\text{Fe}^{III}(\text{H}_2\text{O})_6]^{3+}$  has a magnetic moment of 5.92 B.M. Explain.
11. Which of the complexes use  $d$ -orbital of the metal/metal ion in hybridisation?  
 (a)  $\text{MnO}_4^-$  (b)  $\underline{\text{Ni}}(\text{CO})_4$   
 (c)  $[\underline{\text{Ni}}(\text{CN})_4]^{2-}$  (d)  $[\underline{\text{Fe}}(\text{H}_2\text{O})_6]^{3+}$   
 (e)  $[\underline{\text{Fe}}(\text{CN})_6]^{3-}$
12. What is the EAN (effective atomic number) of the underlined atoms in the following complexes?  
 (a)  $[\underline{\text{Fe}}(\text{CN})_6]^{4-}$  (b)  $[\underline{\text{Cr}}(\text{en})_3]^{3+}$   
 (c)  $\underline{\text{Ni}}(\text{CO})_4$  (d)  $[\underline{\text{Fe}}(\text{H}_2\text{O})_6]^{2+}$

[Hint : EAN = Z(atomic no.) - oxid no. + 2 × (CN), CN is coordination number]

13. Match the geometry (given in column A) with the complexes (given in column B) in :

| A                  | B                                   |
|--------------------|-------------------------------------|
| (I) octahedral     | (a) $[\text{Ni}(\text{CN})_4]^{2-}$ |
| (II) square planar | (b) $[\text{Fe}(\text{CN})_6]^{4-}$ |
| (III) tetrahedral  | (c) $\text{Ni}(\text{CO})_4$        |

14. Calculate magnetic moment  $[= \sqrt{N(N+2)} \text{ BM}]$  where  $N$  = number of unpaired electrons] of the underlined atoms in

- (a)  $\text{Ni}(\text{CO})_4$  (b)  $[\text{Fe}(\text{CN})_6]^{4-}$   
(c)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  (d)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

15. Explain the term 'Lanthanide contraction.'

16. Which is larger in each pair ?

- (a)  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  (b)  $\text{Ni}$  and  $\text{Ni}^{2+}$   
(c)  $\text{Nb}^{3+}$  and  $\text{Ta}^{3+}$  (d)  $\text{Y}^{3+}$  and  $\text{La}^{3+}$   
(e)  $\text{Cu}$  and  $\text{Zn}$  (f)  $\text{Cu}$  and  $\text{Ni}$   
(g)  $\text{I}^-$  and  $\text{I}^+$

17. Due to 'lanthanide contraction', second and third row transition elements (called 4d and 5d series respectively) have similar radii. What are the other properties do you think would be similar?

## Answers

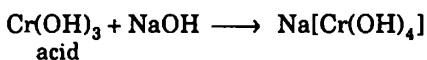
1. (a) 0 (b) +6 (c) +6 (d) +6 (e) +3 (f) +2

2. (a)  $[\text{Ar}]3d^8 4s^2$  (b)  $[\text{Ar}]3d^3$  (c)  $[\text{Ar}]3d^2$  (d)  $[\text{Ar}]3d^3$

3.  $\text{Cr}(\text{OH})_2 < \text{Cr}(\text{OH})_3 < \text{CrO}_2(\text{OH})_2$

Acid strength increases with polarity of the bond which increases with increase in oxidation state.

4.  $\text{Cr}(\text{OH})_3 + 3\text{HCl} \longrightarrow \text{CrCl}_3 + 3\text{H}_2\text{O}$   
base



5. (i)  $E^\circ = 0.46 \text{ V}$  spontaneous

- (ii)  $E^\circ = -1.10 \text{ V}$  non-spontaneous

- (iii)  $E^\circ = -1.56 \text{ V}$  non-spontaneous

6.  $\Delta H = 2300 \text{ kJ mol}^{-1}$  (Add all the reactions to get the desired reaction)

7. (a)  $\text{K}_2\text{PtCl}_6$  (b)  $[\text{Ni}(\text{CN})_4]^{2-}$  (c)  $\text{PtCl}_4$  (d)  $\text{NiCl}_2$

8. because of formation of oxide layer

9. (a)  $2\text{Cr} + 6\text{H}^+ \longrightarrow \text{Cr}^{3+} + 3\text{H}_2$

- (b)  $\text{Zn} + 2\text{H}^+ \longrightarrow \text{Zn}^{2+} + \text{H}_2$

- (c)  $\text{Cu} + 2\text{H}^+ \longrightarrow \text{no reaction}$

- (d)  $\text{Fe} + 2\text{H}^+ \longrightarrow \text{Fe}^{2+} + \text{H}_2$

10.  $[\text{Fe}(\text{CN})_6]^{3-}$  has one unpaired electron ( $d^2sp^3$  hybridised  $\text{Fe}^{3+}$ )

$$\text{Magnetic moment} = \sqrt{N(N+2)} \text{ BM}$$

$$= \sqrt{1(1+2)} \text{ BM}$$

$$= \sqrt{3} = 1.73 \text{ BM}$$

while  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  has five unpaired electrons ( $sp^3d^2$  hybridised  $\text{Fe}^{3+}$ ).

$$\text{Magnetic moment} = \sqrt{5(5+2)} = 35$$

$$= 5.92 \text{ BM}$$

Note : Magnetic moment =  $\sqrt{N(N+2)} \text{ BM}$ , where  $N$  = number of unpaired electrons

11. (a)  $\text{MnO}_4^-$   $sp^3$

- (b)  $\text{Ni}(\text{CO})_4$   $sp^3$

- (c)  $[\text{Ni}(\text{CN})_4]^{2-}$   $dsp^2$

- (d)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$   $sp^3d^2$

- (e)  $[\text{Fe}(\text{CN})_6]^{3-}$   $d^2sp^3$

hence (c), (d), (e) use  $d$ -orbital in bonding.

12. (a) 36 (b) 33 (c) 36 (d) 36

13. A B

- I (b)

- II (a)

- III (c)

| 14. Complex | Unpaired electrons ( $N$ ) | Magnetic moment<br>$= \sqrt{N(N+2)} \text{ BM}$ |
|-------------|----------------------------|-------------------------------------------------|
| (a)         | 0                          | 0                                               |
| (b)         | 0                          | 0                                               |
| (c)         | 5                          | $\sqrt{35} \text{ BM}$                          |
| (d)         | 1                          | $\sqrt{3} \text{ BM}$                           |

15. There is a steady decrease in the radii as the atomic number of the lanthanide element increases. It is because, for every additional proton in a nucleus, the corresponding electron goes into 4f-shell which is too diffused to screen the nucleus as effectively as more localised inner shell. Hence, the attraction of the nucleus for the outermost electrons increases steadily with the atomic number of the lanthanides. This contraction in size is quite regular. This is called **Lanthanide contraction**.

16. (a)  $\text{Fe}^{2+} > \text{Fe}^{3+}$  (b)  $\text{Ni} > \text{Ni}^{2+}$  (c)  $\text{Nb}^{3+} = \text{Ta}^{3+}$

- (d)  $\text{Y}^{3+} < \text{La}^{3+}$  (e)  $\text{Cu} < \text{Zn}$  (f)  $\text{Cu} > \text{Ni}$  (g)  $\text{I}^- > \text{I}^+$

17. Lattice energies, solvation energies and ionisation energies would be similar.

## Compounds

### Potassium Dichromate ( $K_2Cr_2O_7$ )

#### Preparation

$K_2Cr_2O_7$  is obtained from chromite ore ( $FeCr_2O_4$ ) in following steps:

|            |                                                                                                                                                                                                                                           |                                                                                                                                        |
|------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|
| Step I :   | Chromite ore is fused with molten $Na_2CO_3$ in the presence of air when $Na_2CrO_4$ and $Fe_2O_3$ are formed. $Fe_2O_3$ is water insoluble while $Na_2CrO_4$ is water soluble hence, separation is done.                                 | $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \xrightarrow{1100^\circ C} 8Na_2CrO_4 + Fe_2O_3 + 8CO_2 \uparrow$<br>water soluble      water insoluble |
| Step II :  | Aqueous solution of $Na_2CrO_4$ is acidified when $Na_2Cr_2O_7$ is formed.                                                                                                                                                                | $2Na_2CrO_4 + H_2SO_4 \xrightarrow{dil.} Na_2Cr_2O_7 + Na_2SO_4 + H_2O$                                                                |
| Step III : | Sodium dichromate ( $Na_2Cr_2O_7$ ) is more soluble and less stable than $K_2Cr_2O_7$ hence, $Na_2Cr_2O_7$ changes to $K_2Cr_2O_7$ on reaction with KCl. On cooling concentrated solution of $K_2Cr_2O_7$ , orange crystals are obtained. | $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 \downarrow + 2NaCl$<br>orange crystals                                                  |

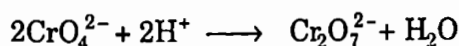
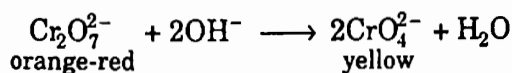
#### Properties

##### Solubility

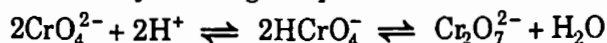
- It exists as orange-red crystals (m.p.  $398^\circ C$ ) and is moderately soluble in cold water but freely soluble in hot water.

##### Behaviour in acid and base

- In alkaline solution (pH > 7), orange colour of  $Cr_2O_7^{2-}$  (dichromate ion) changes to yellow colour due to formation of  $CrO_4^{2-}$  (chromate ion) and again yellow colour changes to orange colour in acid medium (pH < 7):



Thus  $CrO_4^{2-}$  and  $Cr_2O_7^{2-}$  exist in equilibrium and are interconvertible by altering the pH of the solution :



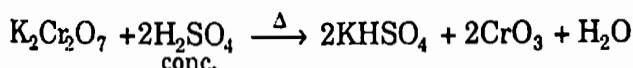
##### Effect of heat

- $4K_2Cr_2O_7 \xrightarrow{\Delta} K_2CrO_4 + 2Cr_2O_3 + 3O_2$
- $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + \underset{\text{green}}{Cr_2O_3} + 4H_2O$

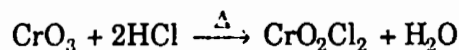
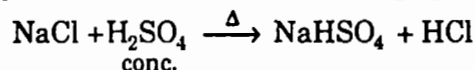
Once this reaction starts, it will keep going at a reasonable rate. Also a small amount of it gives a much larger volume of  $N_2(g)$  along with  $Cr_2O_3$  (green). Both features of the reaction lead to it being used in indoor fireworks.

##### Chromyl chloride test

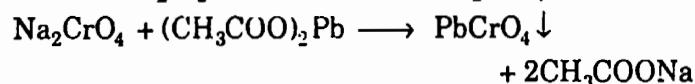
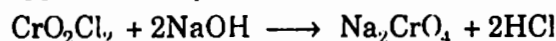
- $K_2Cr_2O_7$  when heated with conc.  $H_2SO_4$  and soluble chloride (like NaCl, KCl), gives deep red vapours of  $CrO_2Cl_2$  (chromyl chloride).



Chromium (VI) oxide (also called chromium trioxide) is red, crystalline compound. It precipitates when conc.  $H_2SO_4$  is added to conc solution of  $K_2Cr_2O_7$ .



$CrO_2Cl_2$  (chromyl chloride) when passed into aqueous NaOH solution, yellow colour solution of  $Na_2CrO_4$  is obtained. This on reaction with  $(CH_3COO)_2Pb/CH_3COOH$  gives yellow ppt of  $PbCrO_4$ :

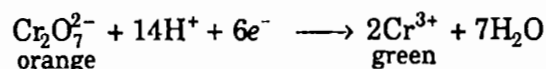


This test called 'Chromyl-Chloride Test' is used to identify  $Cl^-$  in inorganic salt-analysis.

$CrO_2Cl_2$  is an acid chloride and is analogous to  $SO_2Cl_2$  (sulphuryl chloride),

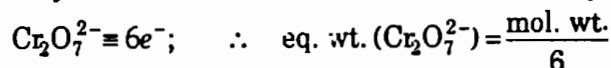
##### Oxidising agent

- $Cr_2O_7^{2-}$  is a good oxidising agent in acidic medium



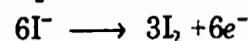
$$E^\circ = 1.33 \text{ V (A)}$$

The reaction is spontaneous ( $E^\circ > 0$ ) and  $Cr_2O_7^{2-}$  is used as a primary standard in volumetric (titrimetric) analysis.

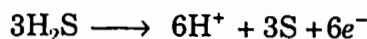


Following reactions are affected by  $Cr_2O_7^{2-}/H^+$  and solution turns green due to formation of  $Cr^{3+}$  (green):

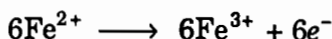
(a)  $I^-$  is oxidised to  $I_2$



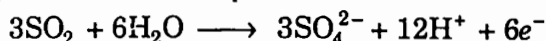
(b)  $\text{H}_2\text{S}$  is oxidised to S



(c)  $\text{Fe}^{2+}$  is oxidised to  $\text{Fe}^{3+}$

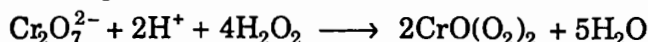


(d)  $\text{SO}_2$  is oxidised to  $\text{SO}_4^{2-}$

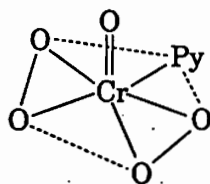
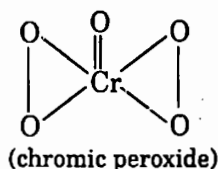


(Use equation (A) to write complete reaction)

(e) When  $\text{H}_2\text{O}_2$  is added to an acidified solution of a dichromate [or any other Cr(VI) species], a complicated reaction occurs. The products depend on the pH and the concentration of Cr(VI) ion :



A deep blue-violet coloured peroxo compound  $\text{CrO}(\text{O}_2)_2$ , called chromic peroxide is formed. This decomposes rapidly in aqueous solution into  $\text{Cr}^{3+}$  and oxygen. The peroxo compound can be extracted into ether, where it is stable; it reacts with pyridine forming the adduct :  $\text{Py} \cdot \text{CrO}(\text{O}_2)_2$



### DEEP Focus

In less acidic solution,  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{O}_2$  give salts which are violet coloured and diamagnetic due to formation of  $[\text{CrO}(\text{O}_2)(\text{OH})]^-$ .

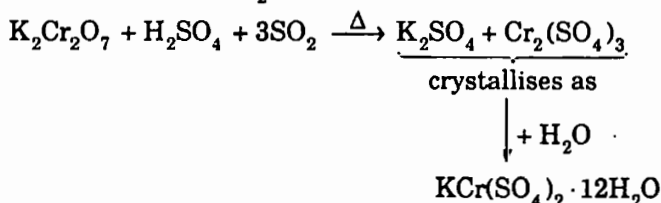
In alkaline solution with 30%  $\text{H}_2\text{O}_2$ , a red-brown compound  $\text{K}_3\text{CrO}_8$  is formed. It is tetraperoxo species  $[\text{Cr}(\text{O}_2)_4]^{3-}$  and thus contains Cr (V) ion.

In ammoniacal solution  $(\text{NH}_3)_3\text{CrO}_4$ , a dark red-brown compound with Cr (IV) ion is formed.

### $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ — Chrome alum

It is a deep purple compound used for leather tanning.

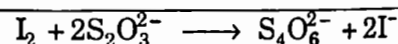
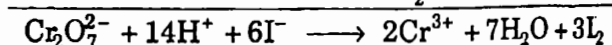
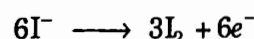
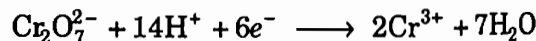
- Chrome alum is obtained when acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution is saturated with  $\text{SO}_2$ :



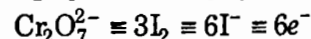
### Estimation of $\text{Cr}_2\text{O}_7^{2-}$

$\text{K}_2\text{Cr}_2\text{O}_7$  can be estimated volumetrically by a iodometric titration.

Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  is treated with KI and liberated  $\text{I}_2$  is titrated using hypo ( $\text{Na}_2\text{S}_2\text{O}_3$ ) solution with starch indicator.



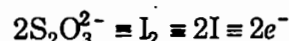
Thus,



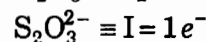
$\therefore$

$$1\text{e}^- \equiv 1\text{I} = \frac{\text{Cr}_2\text{O}_7^{2-}}{6}$$

$$\text{Equivalent weight of } \text{K}_2\text{Cr}_2\text{O}_7 = \frac{\text{molecular weight}}{6} = \frac{294}{6} = 49$$

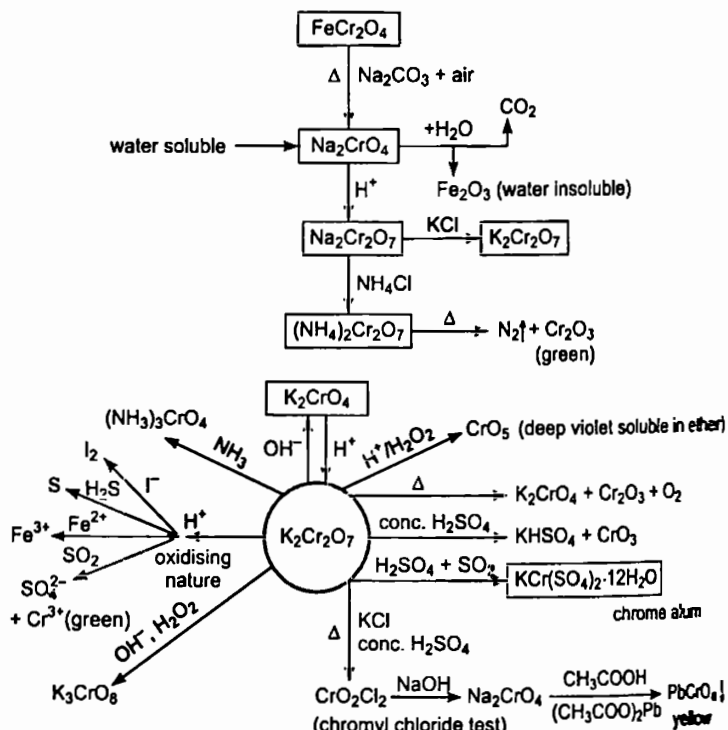
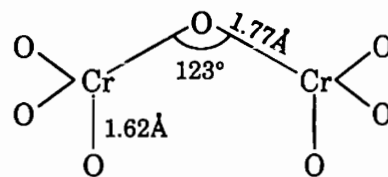


$\therefore$



$$\text{Equivalent weight of } \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = \frac{248}{1}$$

- $\text{PbCrO}_4$  — Chrome yellow
- $\text{PbCrO}_4 \cdot \text{PbO}$  — Chrome red
- $\text{PbCrO}_4 + [\text{FeFe}(\text{CN})_6]^-$  — Chrome green
- Prussian blue
- $\text{Zn}(\text{OH})_2 \cdot \text{ZnCrO}_4 \cdot \text{H}_2\text{O}$  — Yellow
- $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  — Guignete's green
- $\text{CrO}_3$  — Orange (called chromic acid)
- $\text{K}_3[\text{CrO}_8]$  — Red-brown
- $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  — Bright blue
- $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  — Violet
- In  $\text{Cr}_2\text{O}_7^{2-}$  two  $\text{CrO}_3$  units have been joined by O



## Potassium Permanganate (KMnO<sub>4</sub>)

### Preparation

KMnO<sub>4</sub> is prepared from MnO<sub>2</sub> (pyrolusite) in following steps :

**Step I :** MnO<sub>2</sub> is fused with KOH and KClO<sub>3</sub> or KNO<sub>3</sub> when potassium manganate (K<sub>2</sub>MnO<sub>4</sub>) is formed as indicated by its green colour. KClO<sub>3</sub>/KNO<sub>3</sub> acts as oxidising agent.

$$3\text{MnO}_2 + 6\text{KOH} + \text{KClO}_3 \xrightarrow{\Delta} 3\text{K}_2\text{MnO}_4 + \text{KCl} + 3\text{H}_2\text{O}$$

green

**Step II :** The fused mass is extracted with water and solution is green (MnO<sub>4</sub><sup>2-</sup>)

(a) when Cl<sub>2</sub> gas is passed, K<sub>2</sub>MnO<sub>4</sub> is oxidised to KMnO<sub>4</sub> (purple).

$$2\text{K}_2\text{MnO}_4 + \text{Cl}_2 \longrightarrow 2\text{KCl} + 2\text{KMnO}_4$$

greenpurple

(b) MnO<sub>4</sub><sup>2-</sup> can be oxidised to MnO<sub>4</sub><sup>-</sup> electrochemically at anode.

at anode : MnO<sub>4</sub><sup>2-</sup> → MnO<sub>4</sub><sup>-</sup> + e<sup>-</sup>

at cathode : 2H<sup>+</sup> + 2e<sup>-</sup> → H<sub>2</sub>

• Strong oxidising agents such as PbO<sub>2</sub> or sodium bismuthate (NaBiO<sub>3</sub>) can also oxidise Mn<sup>2+</sup> to MnO<sub>4</sub><sup>-</sup>.

• MnO<sub>4</sub><sup>2-</sup> is unstable in acidic medium and disproportionates:



• KMnO<sub>4</sub> crystallises as deep purple rhombic prisms.

### DEEP Focus

MnO<sub>4</sub><sup>-</sup> (VII) has 3d<sup>0</sup> electronic configuration in Mn and thus MnO<sub>4</sub><sup>-</sup> would be expected to be colourless, but colour arises due to charge transfer by oxygen to Mn and thus one of the oxygen is O<sup>-</sup> and Mn changes from +VII to +VI (with one unpaired electron in 3d) hence, coloured.

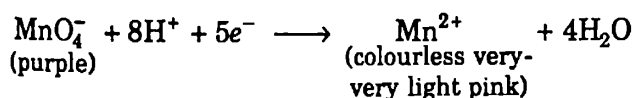
• It is isomorphous with KClO<sub>4</sub>, potassium perchlorate; highly soluble in water :

### Effect of heat

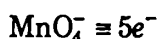


### Oxidising agent

I. KMnO<sub>4</sub> is a good oxidising agent; it finds use in volumetric analysis as secondary standard in the estimation of Fe<sup>2+</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, H<sub>2</sub>O<sub>2</sub> etc. in acidic medium:



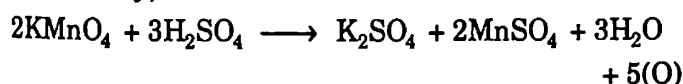
The purple colour of MnO<sub>4</sub><sup>-</sup> acts as its own indicator (self) in titrations



Thus, equivalent weight of MnO<sub>4</sub><sup>-</sup>

$$= \frac{\text{mol. wt.}}{5} \text{ in acidic medium.}$$

Alternately,



$$2\text{KMnO}_4 \equiv 5(\text{O}) \text{ taking weight as } 16.$$

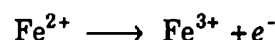
$$\equiv 10(\text{O}) \text{ taking weight as } 8.$$

$$\frac{\text{KMnO}_4}{5} = 1(\text{O})$$

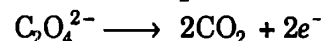
$$\therefore \text{Eq. wt. of KMnO}_4 \text{ in acidic medium} = \left( \frac{\text{mol. wt.}}{5} \right)$$

Some oxidation reactions (using MnO<sub>4</sub><sup>-</sup>/H<sup>+</sup>) are :

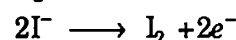
(a) Fe<sup>2+</sup> is oxidised to Fe<sup>3+</sup>



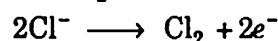
(b) Oxalate is oxidised to CO<sub>2</sub>,



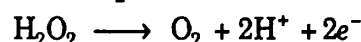
(c) I<sup>-</sup> is oxidised to I<sub>2</sub>



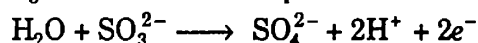
(d) Cl<sup>-</sup> is oxidised to Cl<sub>2</sub>



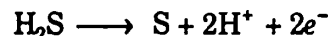
(e) H<sub>2</sub>O<sub>2</sub> is oxidised to O<sub>2</sub>



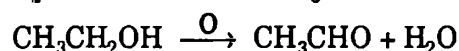
(f) SO<sub>2</sub> (SO<sub>3</sub><sup>2-</sup>) is oxidised to SO<sub>4</sub><sup>2-</sup>



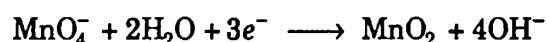
(g) H<sub>2</sub>S is oxidised to S



(h) CH<sub>3</sub>CH<sub>2</sub>OH is oxidised to CH<sub>3</sub>CHO



II. In dilute alkaline solution, MnO<sub>2</sub> is formed.

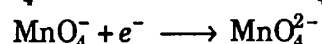
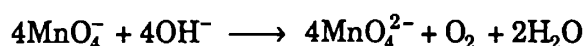


$$\text{Eq. wt. (in basic medium)} = \left( \frac{\text{mol. wt.}}{3} \right)$$

H<sub>2</sub>O<sub>2</sub> is oxidise to O<sub>2</sub>



III. In very strong base, and with an excess of MnO<sub>4</sub><sup>-</sup>, however manganate ion (MnO<sub>4</sub><sup>2-</sup>) is formed.

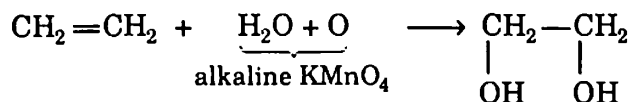


and  $\text{eq. wt.} = \frac{\text{mol wt.}}{1}$

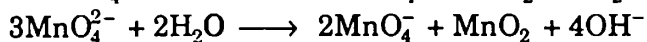
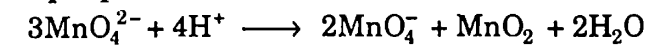
Thus, equivalent weight of KMnO<sub>4</sub> varies with medium.



Alkaline  $\text{KMnO}_4$  is called **Baeyer's reagent** and is used to test **unsaturation** in an organic compound, when it decolorises  $\text{KMnO}_4$ .

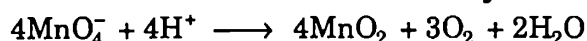


In dilute alkali, water or acidic solutions,  $\text{MnO}_4^{2-}$  again disproportionates:



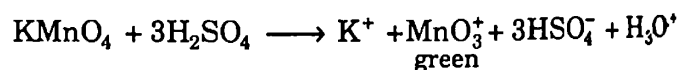
### Stability in acidic medium

- Permanganate solutions are intrinsically unstable in acidic solution, and decompose slowly. Decomposition is catalysed by sunlight, so  $\text{KMnO}_4$  solutions should be stored in dark bottles and they must be standardised at the moment of its use in volumetric analysis.

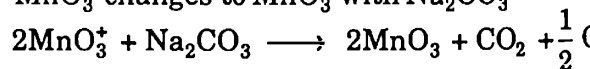


### With conc. $\text{H}_2\text{SO}_4$

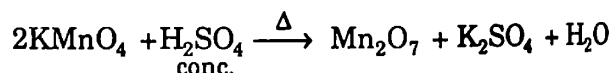
- If a small amount of  $\text{KMnO}_4$  is added to concentrated  $\text{H}_2\text{SO}_4$ , a green solution containing  $\text{MnO}_3^+$  ions is formed:



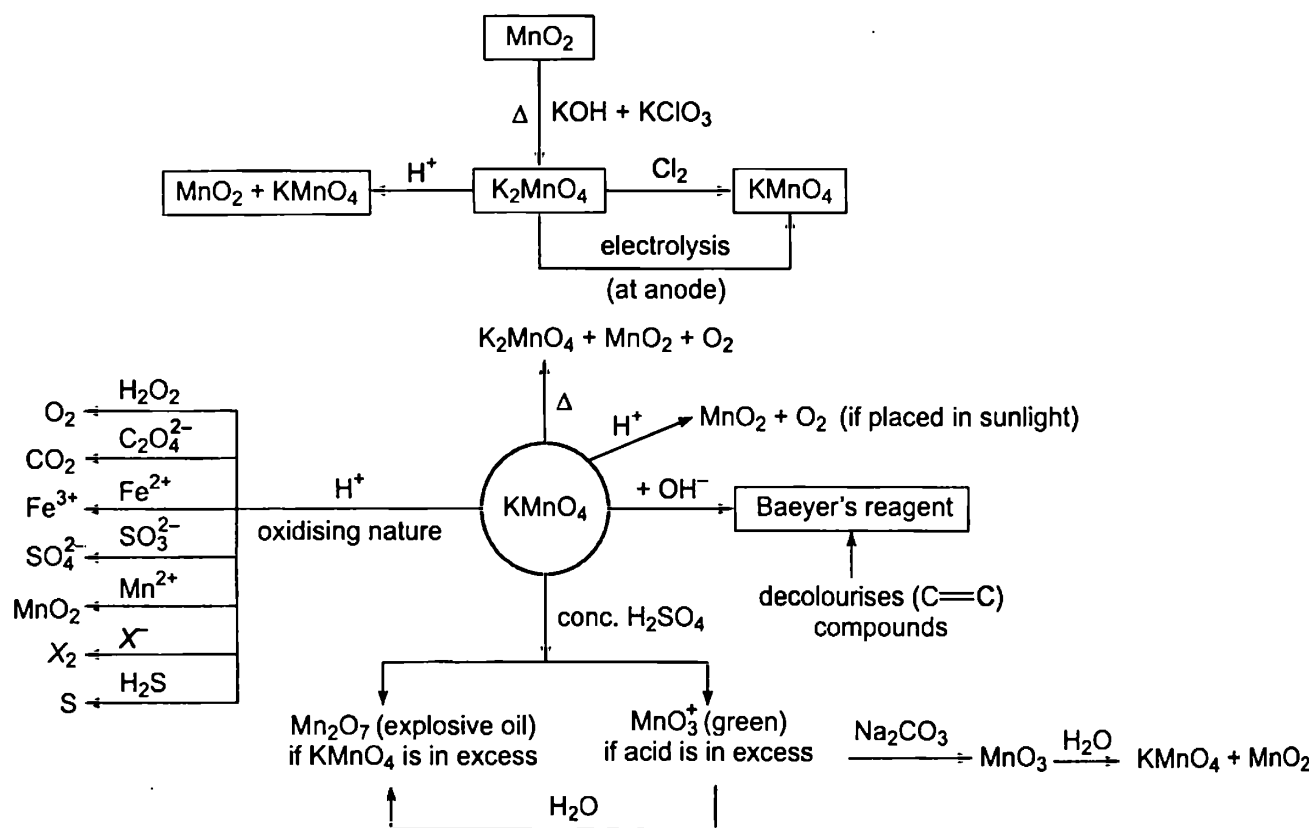
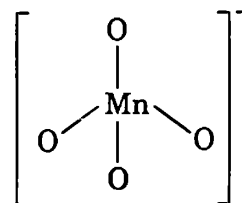
$\text{MnO}_3^+$  changes to  $\text{MnO}_3$  with  $\text{Na}_2\text{CO}_3$



If  $\text{KMnO}_4$  is in excess, an explosive oil  $\text{Mn}_2\text{O}_7$  is formed:



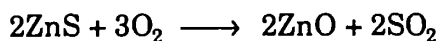
$\text{MnO}_4^-$  has following structure



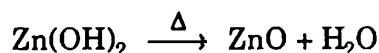
## Zinc Oxide (ZnO) Zinc white

### Preparation

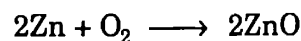
- $\text{ZnO}$  is formed when  $\text{ZnS}$  is oxidised :



$\text{Zn}(\text{OH})_2$  on strongly heating gives  $\text{ZnO}$  :



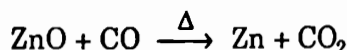
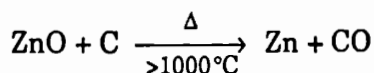
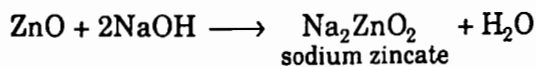
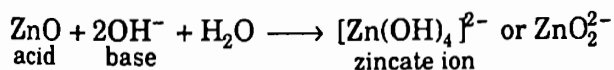
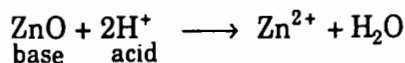
Zinc on burning in air gives  $\text{ZnO}$  (commercial method)



### Properties

- $\text{ZnO}$  is white when it is cold, a property that has given it a use as a pigment in paints. However, it **changes colour, when hot, to a pale yellow**. This is due to **change in the structure of lattice**.

- ZnO is soluble both in acid and alkali and is thus amphoteric in nature :



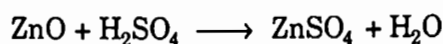
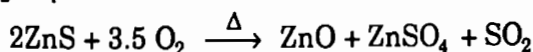
- It is preferred to white lead as it is not blackened by  $\text{H}_2\text{S}$ . It is also used in medicine and in the preparation of **Rinmann's green** ( $\text{ZnCo}_2\text{O}_4$ ).

## Zinc Sulphate ( $\text{ZnSO}_4$ )

### Preparation

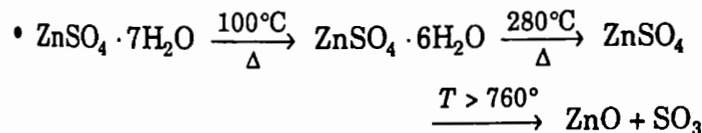
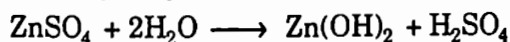
- $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (also called white vitriol) is formed:
  - by decomposing  $\text{ZnCO}_3$  with dil.  $\text{H}_2\text{SO}_4$ 

$$\text{ZnCO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{ZnSO}_4 + \text{H}_2\text{O} + \text{CO}_2$$
  - by heating  $\text{ZnS}$  (zinc blende) in air at lower temperature and dissolving the product in dil.  $\text{H}_2\text{SO}_4$



### Properties

- Highly soluble in water and solution is acidic in nature due to hydrolysis



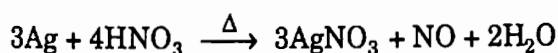
It slowly effloresces when exposed to air.

- It is isomorphous with Epsom salt and used in the manufacture of **lithophone** (which is a mixture of  $\text{BaS}$  +  $\text{ZnSO}_4$  and is used as white pigment).

## Silver Nitrate (Lunar Caustic) $\text{AgNO}_3$

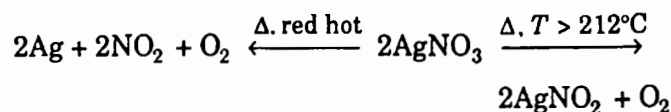
### Preparation

- When Ag is heated with dil.  $\text{HNO}_3$ ,  $\text{AgNO}_3$  is formed. Crystals separate out on cooling the concentrated solution of  $\text{AgNO}_3$ .

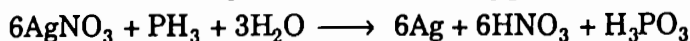
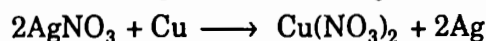


### Properties

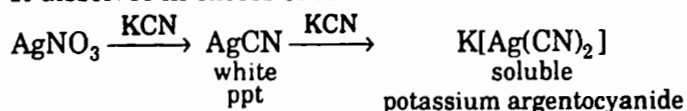
- Colourless crystalline compound soluble in  $\text{H}_2\text{O}$  and alcohol; m.p.  $212^\circ\text{C}$
- When exposed to light, it decomposes hence, stored in a brown coloured bottle :



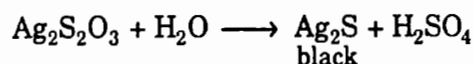
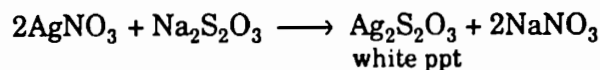
- It is reduced to metallic Ag by more electropositive metals like Cu, Zn, Mg and also by  $\text{PH}_3$ .



- It dissolves in excess of KCN :

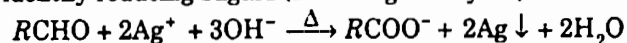


- $\text{AgNO}_3$  gives white precipitate with  $\text{Na}_2\text{S}_2\text{O}_3$ ; white precipitate changes to black.

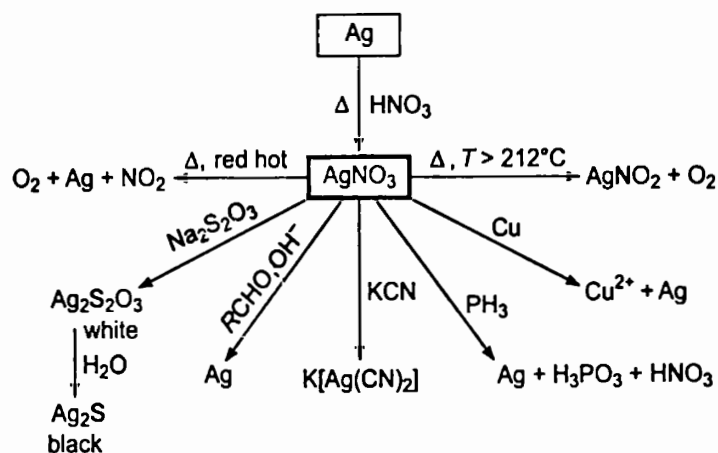


### DEEP Focus

- It possesses powerful corrosive action on organic tissues, which it turns black especially in presence of light. The blackening is due to finely divided metallic silver, reduced by the organic matter.
- Ammoniacal  $\text{AgNO}_3$  is called **Tollen's reagent** and is used to identify reducing sugars (including aldehydes) :

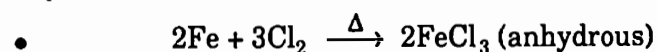


It is called '**silver mirror test**' of aldehydes and reducing sugar (like glucose, fructose).



## Ferric Chloride ( $\text{FeCl}_3$ )

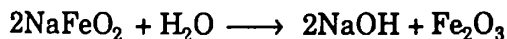
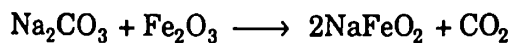
### Preparation





### Fusion with $\text{Na}_2\text{CO}_3$

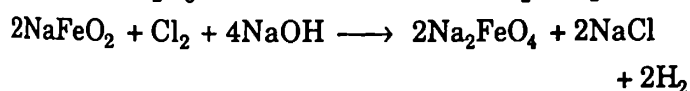
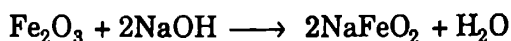
- Fusion of  $\text{Fe}_2\text{O}_3$  with  $\text{Na}_2\text{CO}_3$  gives  $\text{NaFeO}_2$  (sodium ferrite) which is hydrolysed to  $\text{Fe}_2\text{O}_3$  and  $\text{NaOH}$  :



(In earlier days this method, called **Lowig Process**, was used to manufacture  $\text{NaOH}$ ).

### With $\text{Cl}_2$

- If  $\text{Cl}_2$  gas is passed into an alkaline solution of hydrated ferric oxide, a red purple solution is formed containing the ferrate ion  $[\text{FeO}_4]^{2-}$ .

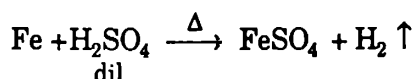
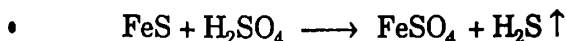


### DEEP Focus

$\text{Na}_2\text{FeO}_4$  can also be obtained by oxidation of  $\text{Fe}_2\text{O}_3$  with  $\text{NaOCl}$  (sodium hypochlorite).  $\text{Na}_2\text{FeO}_4$  has  $\text{Fe}(+\text{VI})$  and is a strong oxidising agent (like  $\text{KMnO}_4$ ).

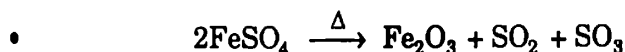
### Ferrous Sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ – Green Vitriol)

#### Preparation



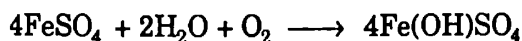
$\text{FeSO}_4$  solution is concentrated when pale green crystals are obtained.

#### Effect of heat



### Atmospheric oxidation

- Anhydrous  $\text{FeSO}_4$  is colourless/white. On exposure to atmosphere it turns brownish-yellow due to formation of basic ferric sulphate :



- $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  is isomorphous with  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (white vitriol) and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (Epsom salt).

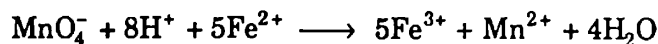
### Hydrolysis

- Aqueous solution of  $\text{FeSO}_4$  is acidic due to hydrolysis of  $\text{Fe}^{2+}$  :

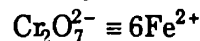
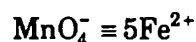
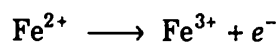
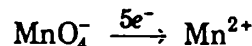


### Oxidation

- Acidified  $\text{MnO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  oxidise  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  :



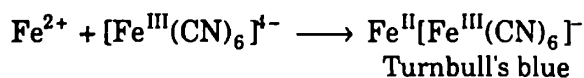
Thus,  $\text{MnO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  can be used to estimate  $\text{Fe}^{2+}$  salts by volumetric method in acidic medium.



Similarly,

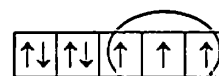
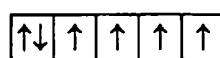
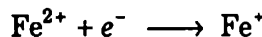
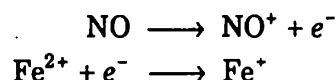
### Detection

- $\text{Fe}^{2+}$  salts form blue precipitate of Turnbull's blue with  $\text{K}_3[\text{Fe}(\text{CN})_6]$ . Turnbull's blue is used as pigment in ink and paint (also refer  $\text{FeCl}_3$ )



### Ring test (for $\text{NO}_3^-$ )

- The complex  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  is formed in the brown ring test for nitrates when freshly prepared  $\text{FeSO}_4$  solution is added to aqueous solution of  $\text{NO}_3^-$  followed by addition of conc.  $\text{H}_2\text{SO}_4$ . The colour is due to charge transfer. Its magnetic moment is approximately 3.873 BM confirming the presence of three unpaired electrons in iron. Thus iron exists as  $\text{Fe}(+\text{I})$  and nitrosyl as  $\text{NO}^+$ .

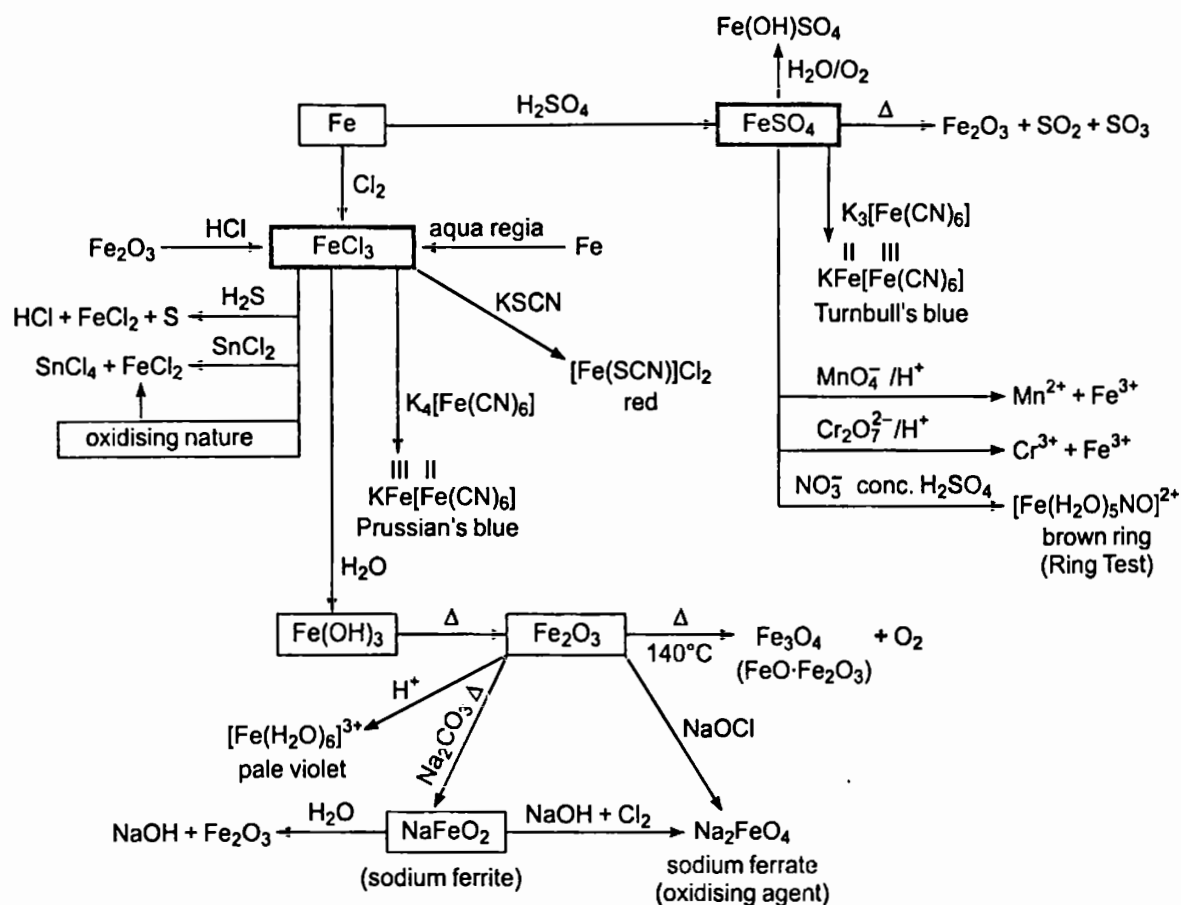


gained  
electron from  
NO

three unpaired  
electrons in  
 $\text{Fe}^+$

$$\begin{aligned} \text{Thus, magnetic moment} &= \sqrt{N(N+2)} \text{ BM} \\ &= \sqrt{15} \\ &= 3.873 \text{ BM} \end{aligned}$$

- Mixture of  $\text{FeSO}_4$  and  $\text{H}_2\text{O}_2$  is used as **Fenton's reagent** for producing hydroxyl radicals and for oxidising alcohols to aldehydes.
- Saturated solution of  $\text{FeSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  on concentration and cooling gives crystals of Mohr's salt,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  which is widely used as **primary standard** for standardisation of  $\text{KMnO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  solutions.

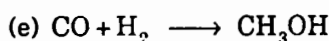
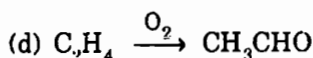
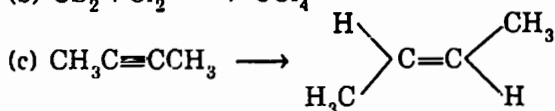
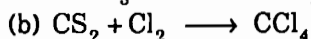
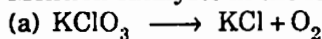


## Target Practice 2

1. Iron(II) oxide is written as  $\overline{\text{FeO}}$ . What does it mean?

.....

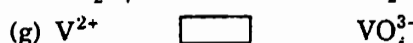
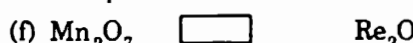
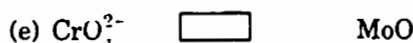
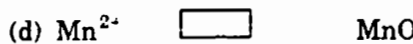
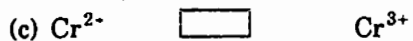
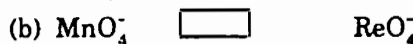
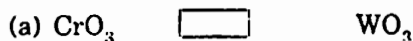
2. Mention catalysts in the following



3. When  $\text{CO}_2$  is passed into aqueous  $\text{K}_2\text{CrO}_4$  (yellow) solution, this changes to orange. This is explained by following reactions

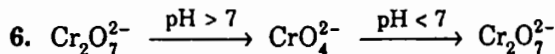
.....

4. Which of the following pairs is more stable?



5.  $\text{Cr}_2\text{O}_3$  is an amphoteric oxide. Thus,

it dissolves in acid forming .....  
and dissolves in base forming .....



Explain the change based on reactions

.....

7. Name the compound which imparts odour in fire-works

.....

8. Write the formulae of

(a) Chromyl chloride .....

(b) Chrome yellow .....

(c) Chrome green .....

(d) Chrome alum .....

9. What is oxidation state of Cr in

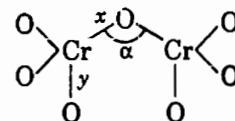
(a)  $\text{CrO}_5$  .....

(b)  $[\text{CrO}_3(\text{OH})]^-$  .....

(c)  $[\text{Cr}(\text{O}_2)_4]^{3-}$  .....

(d)  $\text{CrO}_2\text{Cl}_2$  .....

10. Consider structure of  $\text{Cr}_2\text{O}_7$



State (a) Angle  $\angle \alpha =$  .....

(b) Bond length  $x =$  .....

(c) Bond length  $y =$  .....

11. Alcohol content in a drunkard person can be determined by  $K_2Cr_2O_7$ . Explain in their lines.  
.....  
.....  
.....
12. (a) Lithophone is .....  
(b) Rinmann's green is .....  
(c) Zinc blende is .....  
(d) White vitriol is .....
13. ZnO is converted into ..... in basic medium and into ..... in acidic medium.
14. ZnO is amphoteric. Name two other oxides of *d*-block elements which are amphoteric
- (a) .....  
(b) .....
15. (a) ZnO is white when cold and is yellow when hot. This colour change is due to .....  
(b)  $ZnSO_4 \cdot 7H_2O$  loses  $H_2O$  on exposure to air. This property is called .....
16. Calculate equivalents in one mole each of ..... in following reactions
- one mole =
- (a)  $Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$  ..... equivalents  
(b)  $MnO_4^- \longrightarrow MnO_4^{2-}$  ..... equivalents  
(c)  $MnO_4^- \longrightarrow Mn^{2+}$  ..... equivalents  
(d)  $MnO_4^- \longrightarrow MnO_2$  ..... equivalents

### Answers

1. It is to indicate that ratio of Fe and O atoms is not exactly 1 : 1. Analysis shows that formula varies between  $Fe_{0.94}O$  and  $Fe_{0.84}O$ .
2. (a)  $MnO_2$  (b)  $FeCl_3$  (c)  $Li/NH_3$  (d)  $PdCl_2$   
(e)  $ZnO/CuO$
3.  $CO_2 + H_2O \rightleftharpoons H_2CO_3$   
 $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$   
 $H^+$  change  $K_2CrO_4$  into  $K_2Cr_2O_7$   
$$\underset{\text{yellow}}{2CrO_4^{2-}} + 2H^+ \longrightarrow \underset{\text{orange}}{Cr_2O_7^{2-}} + H_2O$$
4. (a)  $WO_3$  (b)  $ReO_4^-$  (c)  $Cr^{3+}$  (d)  $Mn^{2+}$  (e)  $MoO_4^{2-}$   
(f)  $Re_2O_7$  (g)  $VO_4^{3-}$
5.  $Cr^{3+}$  (acid medium),  $Cr(OH)_4^-$  (basic medium)  
 $pH > 7$  (basic medium)  $pH < 7$  (acidic medium)
6.  $Cr_2O_7^{2-}$  changes to  $CrO_4^{2-}$   $CrO_4^{2-}$  changes to  $Cr_2O_7^{2-}$   
$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$
  
$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$
7.  $(NH_4)_2Cr_2O_7$
8. (a)  $CrO_2Cl_2$  (b)  $PbCrO_4$  (c)  $PbCrO_4 + Fe^{III}[Fe^{II}(CN)_6]^-$   
(d)  $[K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O]$
9. (a)  $Cr = +6$  (b)  $Cr = +4$  (c)  $Cr = +5$  (d)  $Cr = +6$
10. (a)  $\angle \alpha = 123^\circ$  (b)  $x = 1.77 \text{ \AA}$  (c)  $y = 1.62 \text{ \AA}$
11. Drunkard person takes a breath, alcohol content is oxidised to  $CH_3CHO$  by  $K_2Cr_2O_7/H^+$  which in turn is reduced to  $Cr^{3+}$  (green). Formation of green colour indicates alcohol content.
12. (a) Mixture of BaS and  $ZnSO_4$  (b)  $ZnCo_2O_4$   
(c)  $ZnS$  (d)  $ZnSO_4 \cdot 7H_2O$
13.  $[Zn(OH)_4]^{2-}$  or  $ZnO_2^{2-}$  (basic medium);  $Zn^{2+}$  (acidic medium)
14. (a)  $TiO_2$  (b)  $V_2O_5$
15. (a) Change in structure of lattice (b) efflorescence
16. (a) 6 (b) 1 (c) 5 (d) 3  
Change oxidation number per mole

### Practice Exercise 2

1.  $VO^{2+}$  is oxidised to  $VO_2^+$  by  $MnO_4^-$  in acidic medium, which in turn is reduced to  $Mn^{2+}$ . Write balanced equation for this reaction.
2. One of the following oxide is also called chromic acid. Select that one :  $CrO_2$ ,  $Cr_2O_3$ ,  $CrO_3$ ,  $CrO$
3. The red oxide  $CrO_3$  dissolves in water to produce a strongly acidic solution to form orange coloured solution. Solution changes to yellow on making it alkaline. Explain these observations in terms of chemical equations.
4. What is oxidation number of Cr in  
(a)  $CrO_2Cl_2$   
(b)  $CrO_5$  or  $CrO(O_2)_2$   
(c)  $(NH_4)_2Cr_2O_7$   
(d)  $(NH_3)_3CrO_4$  or  $(NH_3)_3Cr(O_2)_2$   
(e)  $[Cr(O_2)_4]^{3-}$
5. Identify A, B, C ... G.  
$$K_2Cr_2O_7 \xrightarrow{KOH} (A) \xrightarrow{Pb(CH_3COO)_2, CH_3COOH} (B)$$
  
$$\downarrow NH_4Cl$$
  
$$(C) \xrightarrow{\Delta} (D) + (E), (E) \xrightarrow{Al, \Delta} (F), (metal) + (G), (oxide)$$
  
gas green
6. Green coloured compound (A)  
$$\downarrow \Delta, NaOH + H_2O_2 \rightarrow (C) \text{ yellow coloured solution}$$
  
$$\downarrow \Delta K_2Cr_2O_7 + \text{conc. } H_2SO_4$$
  
deep-red coloured gas (B)  $\xrightarrow{NaOH}$  yellow coloured solution (C)  
$$(CH_3COO)_2Pb + CH_3COOH \rightarrow (D) \text{ yellow ppt}$$
- Identify A, B, C and D.
7. Explain by reactions.  
(a)  $Mn^{3+}$  disproportionates to  $Mn^{2+}$  and  $MnO_2$  in acidic medium.

- (b)  $\text{MnO}_4^{2-}$  also disproportionates to  $\text{MnO}_2$  and  $\text{MnO}_4^-$  in alkaline medium.  
 (c)  $\text{MnO}_4^-$  oxidises  $\text{Mn}^{2+}$  into  $\text{MnO}_2$  in acidic medium.
8.  $\text{MnO}_4^{2-}$  changes to  $\text{MnO}_2$  and  $\text{MnO}_4^-$  in acidic medium. Calculate equivalent weight of  $\text{MnO}_4^{2-}$ .
9. (a) A qualitative analysis test for  $\text{Mn}^{2+}$  involves its oxidation to  $\text{MnO}_4^-$  in acidic solution by sodium bismuthate,  $\text{NaBiO}_3$ . The bisulphate ion is reduced to  $\text{Bi}^{3+}$ . Write a balanced equation for this test.  
 (b) What happens if  $\text{PbO}_2$  is used instead of  $\text{NaBiO}_3$ ?
10. Give structures of  $\text{MnO}_4^-$  and  $\text{CrO}_4^{2-}$  ions.
11.  $\text{H}_2\text{O}_2$  can be oxidised to  $\text{O}_2$  by  $\text{MnO}_4^-$  in acidic as well as in basic medium.  
 (a) Write reactions.  
 (b) If 100 mL of 1M  $\text{MnO}_4^-$  is used in acidic medium, calculate volume of 1M  $\text{MnO}_4^-$  to be used in basic medium by same  $\text{H}_2\text{O}_2$ .
12. What happens when  $\text{CO}_2$  gas is passed into  $\text{MnO}_4^{2-}$  solution?

13. You have been given  $\text{AlCl}_3$  and  $\text{ZnCl}_2$  solution. To each  $\text{NaOH}$  and  $\text{NH}_4\text{OH}$  are added in excess. What happens?
14.  $\Delta G_f^\circ$  (standard free energy of formation) of  $\text{ZnO}$  and  $\text{CO}$  are  $-318.2 \text{ kJ mol}^{-1}$  and  $-137.3 \text{ kJ mol}^{-1}$ . Is reduction of  $\text{ZnO}$  by carbon possible?
15. Colourless salt (A) gives white ppt (B) with  $\text{NaOH}$ ; ppt (B) dissolves in excess of  $\text{NaOH}$  to form (C). On passing  $\text{H}_2\text{S}$  gas into (C) white ppt (D) appears. (A) also gives white ppt (E) with  $\text{AgNO}_3$  solution. Identify (A) to (E).
16. Colourless salt (A)  $\xrightarrow{\Delta}$  (B) + (C) gas. (B) dissolves both in acid and alkali solution. Gas (C) turns lime water milky and acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution green. Ammoniacal solution of (A) gives white ppt (D) with  $\text{H}_2\text{S}$  gas. Identify (A), (B), (C) and (D).
17. What is the advantage of using  $\text{ZnO}$  in paints instead of  $\text{Pb}^{2+}$  salts?
18. Compare thermal stability of  $\text{ZnO}$ ,  $\text{CdO}$  and  $\text{HgO}$ .

### Answers

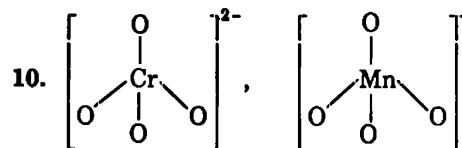
1.  $5\text{VO}^{2+} + \text{MnO}_4^- + \text{H}_2\text{O} \longrightarrow 5\text{VO}_2^+ + \text{Mn}^{2+} + 2\text{H}^+$   
 2.  $\text{CrO}_3$   
 3.  $2\text{CrO}_3 + \text{H}_2\text{O} \longrightarrow \text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+$   
 $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \longrightarrow 2\text{CrO}_4^{2-}$   
 4. (a) VI (b) VI (O = -2, diperoxo = -4) (c) VI (d) IV (e) V  
 (oxidation number of O in peroxide = -1 and in oxide = -2)  
 5. (A):  $\text{K}_2\text{CrO}_4$  (B):  $\text{PbCrO}_4$  (C):  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (D):  $\text{N}_2$   
 (E):  $\text{Cr}_2\text{O}_3$  (F):  $\text{Cr}$  (G):  $\text{Al}_2\text{O}_3$   
 6. (A):  $\text{CrCl}_3$  (B):  $\text{CrO}_2\text{Cl}_2$  (by chromyl chloride test of  $\text{Cl}^-$ )  
 (C):  $\text{Na}_2\text{CrO}_4$  (due to oxidation of  $\text{Cr}^{3+}$  by  $\text{NaOH}/\text{H}_2\text{O}_2$  and due to dissolution of  $\text{CrO}_2\text{Cl}_2$  in  $\text{NaOH}$ )  
 (D):  $\text{PbCrO}_4$

7. (a)  $2\text{Mn}^{3+} + 2\text{H}_2\text{O} \longrightarrow \text{Mn}^{2+} + \text{MnO}_2 + 4\text{H}^+$   
 $\begin{matrix} +3 & & +2 & +4 \end{matrix}$   
 (b)  $3\text{MnO}_4^{2-} + 2\text{H}_2\text{O} \longrightarrow \text{MnO}_2 + 2\text{MnO}_4^- + 4\text{OH}^-$   
 $\begin{matrix} +6 & & +4 & +7 \end{matrix}$   
 (c)  $2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \longrightarrow 5\text{MnO}_2 + 4\text{H}^+$   
 8.  $3\text{MnO}_4^{2-} + 2\text{H}^+ \longrightarrow \text{MnO}_2 + 2\text{MnO}_4^- + 2\text{H}_2\text{O}$   
 $\begin{matrix} +6 & & +4 & +7 \end{matrix}$

It is a disproportionation reaction. In disproportionation reaction, equivalent weight of the species undergoing disproportionation = Eq. wt. (in oxidation) + Eq. wt. (in reduction)

$$\begin{array}{l} \text{MnO}_4^{2-} \longrightarrow \text{MnO}_2 \quad \text{Eq. wt. (redn.)} = \frac{\text{mol. wt.}}{2} \\ \begin{matrix} +6 & & +4 \end{matrix} \\ \text{MnO}_4^{2-} \longrightarrow \text{MnO}_4^- \quad \text{Eq. wt. (oxidn.)} = \frac{\text{mol. wt.}}{1} \\ \begin{matrix} +6 & & +7 \end{matrix} \\ \therefore \text{Eq. wt. of MnO}_4^{2-} = \frac{M}{2} + \frac{M}{1} = \frac{3}{2}M \end{array}$$

9. (a)  $5\text{BiO}_3^- + 2\text{Mn}^{2+} + 14\text{H}^+ \longrightarrow 2\text{MnO}_4^- + 5\text{Bi}^{3+} + 7\text{H}_2\text{O}$   
 (b)  $5\text{PbO}_2 + 2\text{Mn}^{2+} + 4\text{H}^+ \longrightarrow 2\text{MnO}_4^- + 5\text{Pb}^{2+} + 2\text{H}_2\text{O}$



11. (a)  $2\text{MnO}_4^- + 5\text{H}_2\text{O}_2 + 6\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O}$   
 $2\text{MnO}_4^- + 3\text{H}_2\text{O}_2 \longrightarrow 2\text{MnO}_2 + 3\text{O}_2 + 2\text{OH}^- + 2\text{H}_2\text{O}$   
 (b) In acidic medium  $\text{MnO}_4^- \longrightarrow \text{Mn}^{2+}$

$$1\text{M} = 5\text{N}$$

$$\therefore \text{H}_2\text{O}_2 \equiv 100 \text{ mL of } 5\text{N KMnO}_4$$

$$\text{In basic medium } \text{MnO}_4^- \longrightarrow \text{MnO}_2$$

$$1\text{M} = 3\text{N}$$

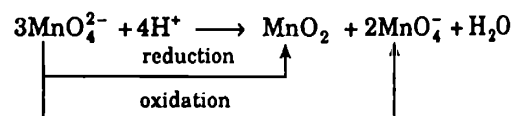
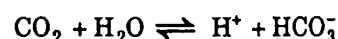
$$\therefore \text{H}_2\text{O}_2 \equiv V \text{ mL of } 3\text{N KMnO}_4$$

$$\therefore NV = 3V$$

$$\therefore 3V = 500$$

$$V = \frac{500}{3} = 166.67 \text{ mL}$$

12. Aqueous  $\text{CO}_2$  releases  $\text{H}^+$  which can convert  $\text{MnO}_4^{2-}$  into  $\text{MnO}_2$  and  $\text{MnO}_4^-$  in a disproportionation reaction.



| 13.                                                 | $\text{AlCl}_3$                                                                                                                                                                                                                                                                                                              | $\text{ZnCl}_2$                                                                                                                                                                                                                                                                                                  |
|-----------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| (a) <b>NaOH added:</b>                              | $\text{Al(OH)}_3$ white precipitate which dissolves in excess of it.<br>$\text{AlCl}_3 + 3\text{NaOH} \longrightarrow \text{Al(OH)}_3 \downarrow + 3\text{NaCl}$ $\text{Al(OH)}_3 + \text{NaOH} \longrightarrow \text{NaAlO}_2 + 2\text{H}_2\text{O}$ <p style="text-align: center;">sodium meta aluminate<br/>(soluble)</p> | $\text{Zn(OH)}_2$ white ppt dissolved in excess of it<br>$\text{ZnCl}_2 + 2\text{NaOH} \longrightarrow \text{Zn(OH)}_2 \downarrow + 2\text{NaCl}$ $\text{Zn(OH)}_2 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{ZnO}_2 + 2\text{H}_2\text{O}$ <p style="text-align: center;">sodium zincate<br/>(soluble)</p> |
| (b) <b><math>\text{NH}_4\text{OH}</math> added:</b> | $\text{Al(OH)}_3$ white ppt; precipitate remains insoluble in excess of it                                                                                                                                                                                                                                                   | $\text{Zn(OH)}_2$ white ppt. but precipitate dissolves in excess of it<br>$\text{Zn(OH)}_2 + 4\text{NH}_4\text{OH} \longrightarrow [\text{Zn(NH}_3)_4]^{2+} + 4\text{H}_2\text{O} + 2\text{OH}^-$ <p style="text-align: center;">soluble</p>                                                                     |

14.  $\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}$   
 $\Delta G^\circ = \Delta G_f^\circ (\text{CO}) - \Delta G_f^\circ (\text{ZnO})$   
 $= -137.3 - (-318.2) = 180.9 \text{ kJ mol}^{-1}$   
 Positive value of  $\Delta G^\circ$  indicates that reaction is non-spontaneous.  
 (However, it is spontaneous above  $1000^\circ\text{C}$ ).
15. (A) :  $\text{ZnCl}_2$  (B) :  $\text{Zn(OH)}_2$  (C) :  $\text{Na}_2\text{ZnO}_2$  (D) :  $\text{ZnS}$

- (E) :  $\text{AgCl}$
16. (A) :  $\text{ZnSO}_4$  (B) :  $\text{ZnO}$  (C) :  $\text{SO}_2$  (D) :  $\text{ZnS}$
17.  $\text{ZnO}$  in white paint by atmospheric  $\text{H}_2\text{S}$  gives  $\text{ZnS}$  (white) but  $\text{Pb}^{2+}$  salts in white paint turns black by atmospheric  $\text{H}_2\text{S}$  due to formation of  $\text{PbS}$ .
18.  $\text{ZnO} > \text{CdO} > \text{HgO}$

## Copper Sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ – Blue Vitriol)

### Preparation

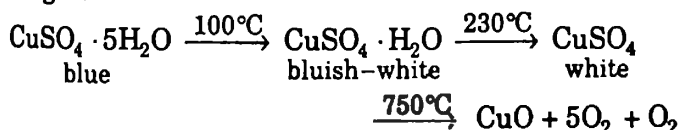
- $\text{CuO} + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{H}_2\text{O}$   
 $2\text{Cu} + 2\text{H}_2\text{SO}_4 + \text{O}_2 \xrightarrow{\Delta} 2\text{CuSO}_4 + 2\text{H}_2\text{O}$   
 On concentration and cooling, blue crystals of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  separate.

### Properties

- The  $\text{Cu(II)}$  ion or cupric ion is written more precisely as  $[\text{Cu(H}_2\text{O)}_4]^{2+}$  when in aqueous solution. It has a bright blue colour. In  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  four of the water molecules are associated with  $\text{Cu}^{2+}$ , and the fifth is hydrogen-bonded to the sulphate ion as well as to the water molecules on the copper ion, hence, this it is written as  $[\text{Cu(H}_2\text{O)}_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ .

### Effect of heat

- When this is heated, it loses its water of hydration in stages:

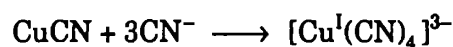
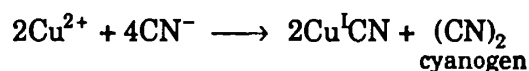


### DEEP Focus

It is the complexing of water molecules to the copper ion that is responsible for the blue colour of the pentahydrate.

### Complex formation with KCN

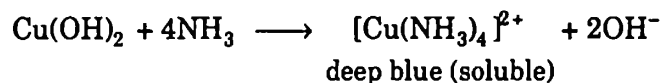
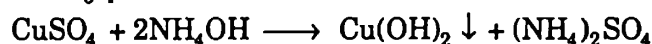
- Addition of  $\text{KCN}$  to  $\text{CuSO}_4$  solution first causes reduction and then precipitates  $\text{CuCN}$  (cuprous cyanide). This reacts with excess  $\text{CN}^-$ , forming a soluble four coordinate complex  $[\text{Cu(CN)}_4]^{3-}$  which is tetrahedral in shape :



$[\text{Cu(CN)}_4]^{3-}$  is a stable complex.  $\text{Cd}^{2+}$  also forms complex  $[\text{Cd(CN)}_4]^{2-}$  but unstable, which ionises to form  $\text{Cd}^{2+}$  and  $\text{CN}^-$ . Thus if  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  both are present,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  both are complexed by  $\text{CN}^-$ . If  $\text{H}_2\text{S}$  gas is passed,  $\text{Cd}^{2+}$  (in unstable  $[\text{Cd(CN)}_4]^{2-}$ ) gives yellow ppt of  $\text{CdS}$ .

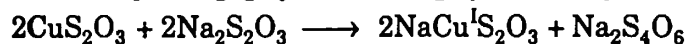
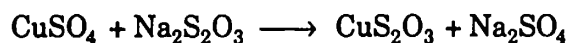
### Complex formation with $\text{NH}_3$

- Addition of aqueous  $\text{NH}_3(\text{aq})$  to  $\text{Cu}^{2+}$  salts give blue ppt of  $\text{Cu(OH)}_2$  which dissolves in excess of  $\text{NH}_3(\text{aq})$  due to the formation of the deep blue complex  $[\text{Cu(NH}_3)_4]^{2+}$  :

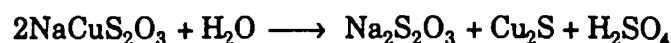


### With hypo

- $\text{CuSO}_4$  solution on reaction with  $\text{Na}_2\text{S}_2\text{O}_3$  gives colourless (white)  $\text{NaCuS}_2\text{O}_3$  due to reduction of  $\text{Cu(II)}$  to  $\text{Cu(I)}$ .



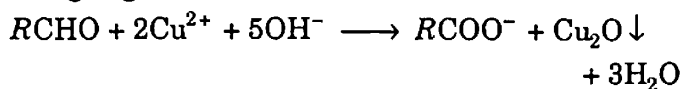
On boiling or in acid solution,  $\text{NaCuS}_2\text{O}_3$  changes to  $\text{Cu}_2\text{S}$ .



- When the copper (II) ion (complexed with tartrate ion) is heated in basic solution with a reducing sugar, such as glucose, the ion is reduced to  $\text{Cu}_2\text{O}$  (brick red precipitate). Mixture of alkaline  $\text{CuSO}_4$  and sodium potassium tartrate is called Fehling's solution and



this test called **Fehling's test** of aldehydes and reducing sugars:

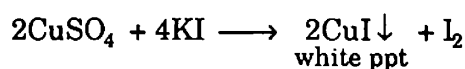


- Benedict's solution contains Cu(II) ion complexed to citrate ion. When it is heated with reducing sugar (as glucose) Cu(II) is reduced to Cu(I) oxide ( $Cu_2O$ ) as in the Fehling's test.

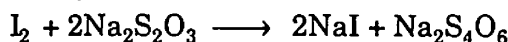
This test called **Benedict's test** is used to test glucose in urine sample.

### Estimation

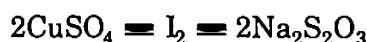
- If excess of KI is added to an acidified solution of  $CuSO_4$  ( $Cu^{2+}$  ions),  $I_2$  is produced by oxidation of  $I^-$  which reduces  $Cu^{2+}$  to CuI (or  $Cu_2I_2$ ):



$I_2$  produced can be determined by titration with hypo solution ( $Na_2S_2O_3$ )

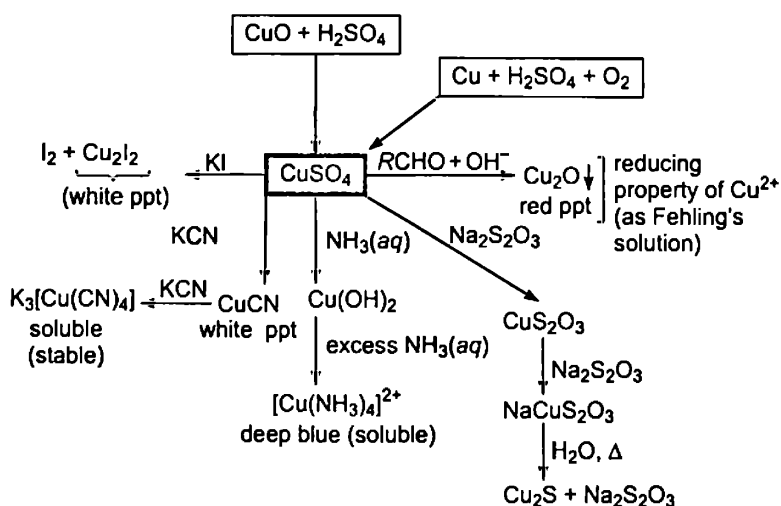


Thus  $CuSO_4$  ( $Cu^{2+}$  salts) can be determined iodometrically:



Eq. wt. of  $CuSO_4$  = mol. wt.

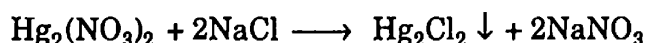
Eq. wt. of  $Na_2S_2O_3$  = mol. wt.



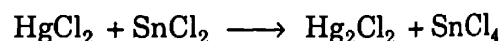
## Mercurous Chloride ( $Hg_2Cl_2$ —Calomel)

### Preparation

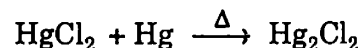
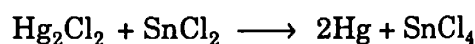
- $Hg_2Cl_2$  (calomel) is formed as white precipitate when soluble chloride (say NaCl) is added to soluble mercurous salt (say  $Hg_2(NO_3)_2$ ):



$Hg_2Cl_2$  is also formed when aqueous  $HgCl_2$  and aqueous  $SnCl_2$  are mixed in 1 : 1 molar ratio, or  $HgCl_2$  is reduced by Hg.

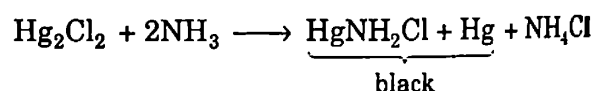


Excess of  $SnCl_2$  would reduce  $Hg_2Cl_2$  to Hg:



### Properties

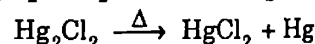
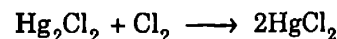
- If treated with aqueous  $NH_3$ , it turns black due to formation of  $Hg(NH_2)Cl \cdot Hg$



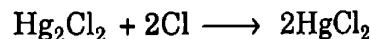
- In  $Hg_2Cl_2$  two Hg atoms are bonded together using the 6s orbitals.

### DEEP Focus

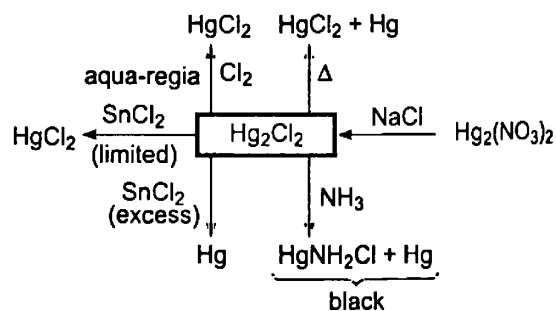
- Mercurous ion is **diamagnetic**; this indicates that there is no unpaired electron, hence, mercurous ion is not  $Hg^+$  but  $Hg_2^{2+}$ :



- It dissolves in aqua-regia forming  $HgCl_2$



It is used in medicine as purgative.



## Mercuric Chloride ( $HgCl_2$ —Corrosive sublimate)

### Preparation

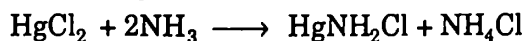
- $Hg + Cl_2 \xrightarrow{\Delta} HgCl_2$
- $Hg + 2Cl$  (aqua regia)  $\longrightarrow HgCl_2$
- $Hg_2Cl_2 + Cl_2 \longrightarrow 2HgCl_2$
- $HgSO_4 + 2NaCl \xrightarrow{MnO_2, \Delta} HgCl_2 + Na_2SO_4$

### Properties

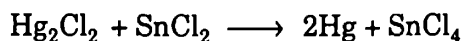
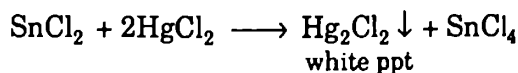
$MnO_2$  prevents formation of  $Hg_2Cl_2$ .

- On account of corrosive property, it is called **corrosive sublimate**.
- Highly soluble in hot water, ether and alcohol.

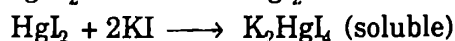
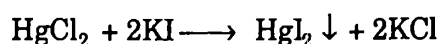
- With aqueous  $\text{NH}_3$ , white ppt of  $\text{HgNH}_2\text{Cl}$  is formed :



- $\text{SnCl}_2$  reduces it to  $\text{Hg}_2\text{Cl}_2$  and then to  $\text{Hg}$  :

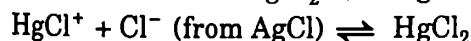
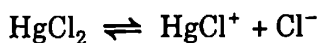


- When treated with  $\text{KI}$ , it forms orange ppt of  $\text{HgI}_2$ , precipitate dissolves in excess of  $\text{KI}$  forming soluble  $\text{K}_2\text{HgI}_4$  (Nessler's reagent) :

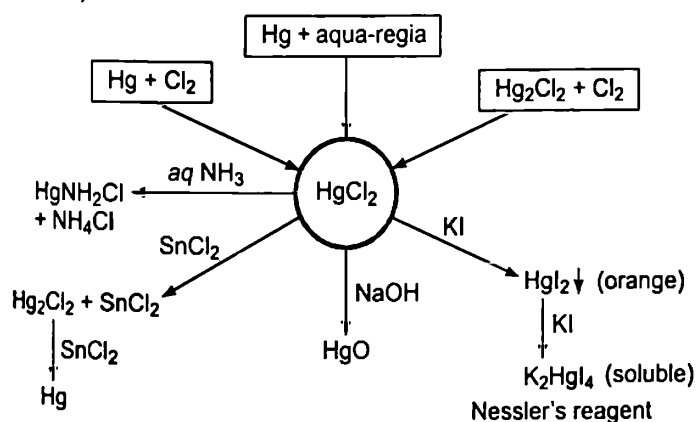


Radioactive tracer technique indicates that in  $\text{HgI}_4^{2-}$  all the iodine atoms are identical.

- It dissolves  $\text{AgCl}$ ,



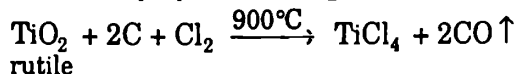
- $\text{HgCl}_2 + 2\text{NaOH} \longrightarrow \text{HgO} + 2\text{NaCl} + \text{H}_2\text{O}$
- It is used in medicine as an antiseptic and dressing skins, furs etc.



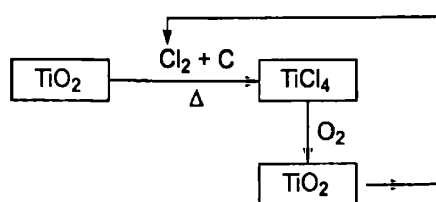
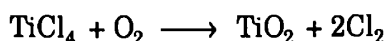
## Titanium (IV) oxide

### Preparation

Rutile ( $\text{TiO}_2$ ) is natural occurring titanium (IV) oxide and is invariably coloured by impurities. Pure  $\text{TiO}_2$  is obtained commercially by **chloride process**

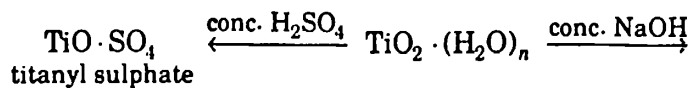


$\text{TiCl}_4$  is volatile and can be separated from impurities.  $\text{TiCl}_4$  is heated with  $\text{O}_2$  at about  $1200^\circ\text{C}$  forming  $\text{TiO}_2$  and  $\text{Cl}_2$ .  $\text{Cl}_2$  is recycled for further conversion of  $\text{TiO}_2$  into  $\text{TiCl}_4$



### Properties

- $\text{TiO}_2$  is amphoteric and thus dissolves in both bases and acids

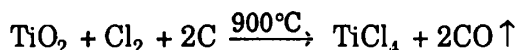


- $\text{TiO}_2$  is used as white pigment in paint. It has three advantages over lead paints
  - it covers better
  - it is non-toxic and
  - it is not blackened by  $\text{H}_2\text{S}$
- $\text{TiO}_2$  is also used for whitening paper and as a filler in plastics and rubber.

## Titanium (IV) Chloride ( $\text{TiCl}_4$ )

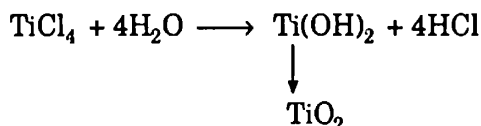
### Preparation

- It is prepared by passing  $\text{Cl}_2$  gas over heated  $\text{TiO}_2$  and C.

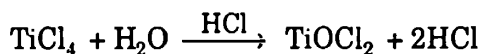


### Properties

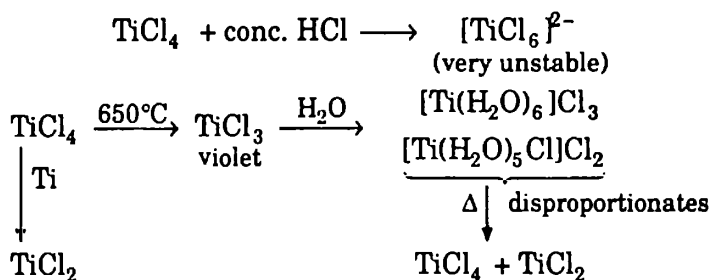
- It is colourless, diamagnetic, covalent fuming liquid.
- It is hydrolysed vigorously by water, giving fumes in moist air



- If hydrolysed in presence of aqueous  $\text{HCl}$ ,  $\text{TiOCl}_2$  is formed



- It acts as a Lewis acid (electron-pair acceptor) forming octahedral complexes:



### DEEP Focus

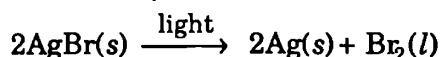
- Solution of  $\text{AlEt}_3$  (triethyl aluminium) and  $\text{TiCl}_4$  in a hydrocarbon solvent (as cyclohexane) react exothermically to form a brown solid called **Ziegler-Natta catalyst**. This catalyst is used for polymerising ethene into polythene.

### Photography

Ordinary black-and-white photographic film consists of a celluloid strip that has been coated with a gelatin emulsion containing silver halides, usually  $\text{AgBr}$ . Photography involves a series of redox reactions (in stages) as given :

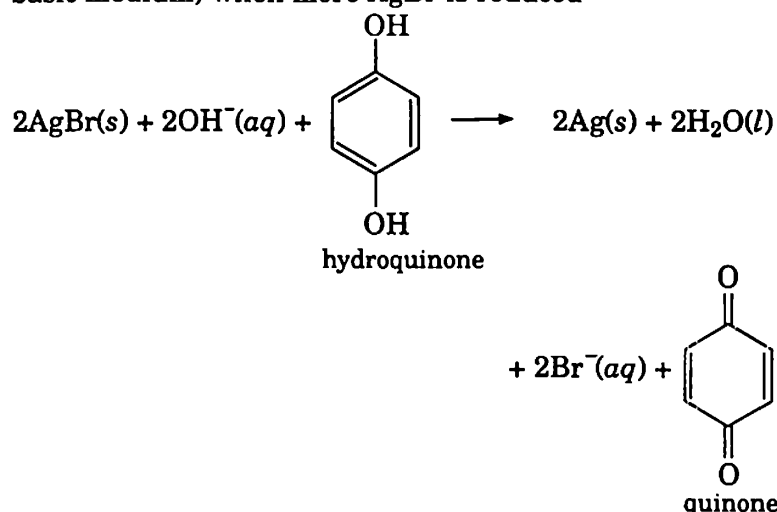
## Exposure

When exposed to light, the surfaces of the AgBr grains turn dark because of light-induced redox reaction in which  $\text{Br}^-$  transfers an electron to  $\text{Ag}^+$ , producing atoms of elemental Ag. (The  $\text{Br}_2$  produced in the reaction reacts with the gelatin emulsion)



## Developing

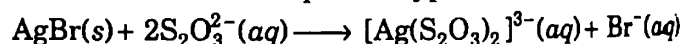
The exposed film is subjected to developing by adding an organic reducing agent (probably hydroquinone in basic medium) when more AgBr is reduced



By carefully monitoring the time period allowed for reduction of the AgBr with hydroquinone it is possible to amplify the latent image on the exposed film and make it visible. At the desired point, further developing is stopped by transferring the film from the basic hydroquinone solution to a weakly acidic one.

## Fixing

Once the image is fully formed, the film is fixed by washing away the remaining unreacted AgBr with a solution of sodium thiosulphate (hypo)

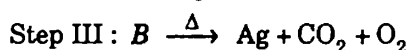
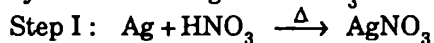


The negative is now ready and can be processed in day-light. Negative is converted to positive by allowing the light to pass through it on to AgBr containing photographic paper which is then treated in a similar way as the negative.

## Target Practice 3

- Name two substances that can reduce  $\text{AgNO}_3$  to Ag  
(a) ..... (b) .....

- Silver coin contains mainly silver. Pure silver is obtained by first dissolving it in  $\text{HNO}_3$  and then other steps



Name A .....

Name B .....

- $\text{AgNO}_3$  is a common reagent of testing halides.

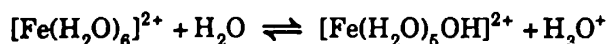
(a)  $\text{AgCl}$  is of ..... ppt soluble in .....

(b)  $\text{AgBr}$  is of ..... ppt partially soluble in .....

(c)  $\text{AgI}$  is of ..... ppt insoluble in .....

- Silver-mirror test is for testing aldehydes reagent used is called ..... and contains .....

- Identify conjugate acid-base pair in the following acid-base reaction



A :                      B :                      C :                      D :

- It is said that  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  consists of *trans*-complex. This *trans*-complex is

- Name two reagent used for testing  $\text{Fe}^{3+}$  and the compounds formed with them

| Reagent    | Compound formed |
|------------|-----------------|
| I : .....  | .....           |
| II : ..... | .....           |

- Following tests are performed with *aq*  $\text{FeCl}_3$  solution.

What is the observation and conclusion?

| Test                          | Observation | Conclusion |
|-------------------------------|-------------|------------|
| (a) $\text{NaHCO}_3$ is added | .....       | .....      |
| (b) Blue litmus is added      | .....       | .....      |
| (c) Red litmus is added       | .....       | .....      |

- Write reaction of manufacturing NaOH in earlier days by Lowig process.

.....

- Name the compound of iron in the +6 oxidation state. How is it prepared.

.....

- Name three non-stoichiometric oxides of iron

.....

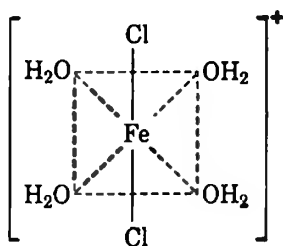
- $\text{Fe}_2\text{O}_3 \cdot (\text{H}_2\text{O})_4$  (freshly precipitated) is dissolved in acid as well as in base in two different test tubes. Write the compounds formed

- (a) in acid .....  
 (b) in base .....
13. Name the compounds with which green vitriol is isomorphous  
 (I) ..... (II) .....
14.  $\text{FeSO}_4$  is generally used freshly prepared. It is due to .....
15.  $\text{FeSO}_4$  or  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  is used as a volumetric reagent for the estimation of oxidising agent like  
 (I) ..... (II) .....
16. Mohr's salt can be estimated by  $\text{MnO}_4^-/\text{H}^+$ , with  $\text{MnO}_4^-$  as self-indicator. How does it work? .....
17. Mohr's salt can be estimated by  $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$ . Name the indicator used .....
18. Name the contents of  
 (a) Fehling solution .....  
 (b) Benedict's solution .....  
 (c) Fenton's reagent .....

19. Compare stability of  
 (a)  $[\text{Cu}(\text{CN})_4]^{2-}$  ☐  $[\text{Cu}(\text{CN})_4]^{3-}$   
 (b)  $[\text{Cd}(\text{CN})_4]^{2-}$  ☐  $[\text{Cu}(\text{CN})_4]^{3-}$
20. Specify the temperature for the following changes  
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \xrightarrow{\text{A: K}} \text{CuSO}_4 \cdot \text{H}_2\text{O} \xrightarrow{\text{B: K}} \text{CuSO}_4$   
 $\text{CuO} \xleftarrow{\text{C: K}}$
21. Give two chemical tests to identify  $\text{Cu}^{2+}$  in laboratory  
 (a) .....  
 (b) .....
22. Calculate moles of  $\text{Na}_2\text{S}_2\text{O}_3$  to react with  $\text{I}_2$  obtained when 0.5 mol of  $\text{CuSO}_4$  reacts with excess of KI. Write balanced equations.  
 .....  
 .....
- (For more problems refer Target Practice 4)

## Answers

1. (a) Cu (b) HCHO  
 2. A :  $\text{Na}_2\text{CO}_3$  B :  $\text{Ag}_2\text{CO}_3$   
 3. (a) White, aqueous  $\text{NH}_3$  (b) Yellow, aqueous  $\text{NH}_3$   
 (c) Yellow,  $\text{NH}_3$   
 4. Tollen's reagent, ammoniacal  $\text{AgNO}_3$   
 5. A : Acid B : Base C : Conjugate base of A  
 D : Conjugate acid of B  
 6.  $[\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$



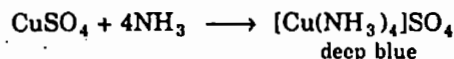
| Reagent                                 | Compounds formed                                                                                                 |
|-----------------------------------------|------------------------------------------------------------------------------------------------------------------|
| I. $\text{K}_4[\text{Fe}(\text{CN})_6]$ | $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$<br>Prussian blue                                  |
| II. KCNS                                | $[\text{Fe}(\text{SCN})]^{2+}$<br>with some<br>$[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$<br>blood red |

| Observation                  | Conclusion                |
|------------------------------|---------------------------|
| (a) $\text{CO}_2$ is evolved | $\text{FeCl}_3$ is acidic |
| (b) turns red                | $\text{FeCl}_3$ is acidic |
| (c) no effect                | .....                     |

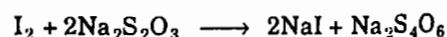
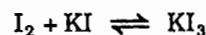
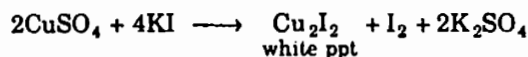
9.  $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3 \longrightarrow 2\text{NaFeO}_2 + \text{CO}_2$   
 $2\text{NaFeO}_2 + \text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{Fe}_2\text{O}_3$   
 Net:  $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{CO}_2$

10.  $\text{Fe}_2\text{O}_3 + 2\text{NaOH} \longrightarrow 2\text{NaFeO}_2 + \text{H}_2\text{O}$   
 $2\text{NaFeO}_2 + \text{Cl}_2 + 4\text{NaOH} \longrightarrow 2\text{Na}_2\text{FeO}_4 + 2\text{NaCl} + 2\text{H}_2$   
 Net :  $\text{Fe}_2\text{O}_3 + 6\text{NaOH} + \text{Cl}_2 \longrightarrow 2\text{Na}_2\text{FeO}_4 + 2\text{NaCl}$   
red purple  
+ 2H<sub>2</sub> + H<sub>2</sub>O
- $\text{Na}_2\text{FeO}_4$  (a strong oxidising agent like  $\text{KMnO}_4$ ) has Fe in +6 state.
11.  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$   
 12. (a)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  pale-violet (b)  $[\text{Fe}(\text{OH})_6]^{3-}$   
 13. I :  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  II :  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$   
(white vitriol) (epsom salt)
14. The fact that on exposure to atmosphere it turns brownish-yellow due to the formation of basic ferric sulphate :  
 $4\text{FeSO}_4 + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 4\text{Fe}(\text{OH})\text{SO}_4$
15. (i)  $\text{KMnO}_4$  (ii)  $\text{K}_2\text{Cr}_2\text{O}_7$   
 16.  $\text{MnO}_4^-$  changes to  $\text{Mn}^{2+}$  (very light pink but appears colourless in aqueous solution) when  $\text{Fe}^{2+}$  is completely oxidised. One additional drop of  $\text{MnO}_4^-$  imparts its own purple-violet colour at the end point.  
 17.  $\text{K}_3[\text{Fe}(\text{CN})_6]$  as external indicator.  $\text{Fe}^{2+}$  solution is tested at the intermediate stages.  $\text{K}_3[\text{Fe}(\text{CN})_6]$  gives blue colour with  $\text{Fe}^{2+}$  but when it is completely oxidised there is no blue colour  
 $\text{Fe}^{2+} + [\text{Fe}(\text{CN})_6]^{3-} \longrightarrow \text{blue}$   
 $\text{Fe}^{3+} + [\text{Fe}(\text{CN})_6]^{3-} \longrightarrow \text{no colour}$
18. (a) Mixture of alkaline  $\text{CuSO}_4$  and sodium potassium tartrate.  
 (b)  $\text{Cu}(\text{II})$  complexed to citrate ion.,  
 (c)  $\text{FeSO}_4$  and  $\text{H}_2\text{O}_2$
19. (a)  $[\text{Cu}(\text{CN})_4]^{2-} < [\text{Cu}(\text{CN})_4]^{3-}$   
 (b)  $[\text{Cd}(\text{CN})_4]^{2-} < [\text{Cu}(\text{CN})_4]^{3-}$
20. A : 373 K B : 503 K C : 1023 K

21. (a) Add aqueous  $\text{NH}_3$  in excess. Formation of deep blue coloured complex indicates  $\text{Cu}^{2+}$

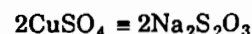


- (b) Add KI solution. Deep brown colour which change to white precipitate on addition of hypo ( $\text{Na}_2\text{S}_2\text{O}_3$ )



Deep brown colour is due to  $\text{KI}_3$  but when hypo is added,  $\text{I}_2$  disappears and  $\text{Cu}_2\text{I}_2$  appears in the form of white precipitate.

22. Based on chemical reaction in 21(b)



$$\therefore \text{Na}_2\text{S}_2\text{O}_3 = 0.5 \text{ mol}$$

## Practice Exercise 3

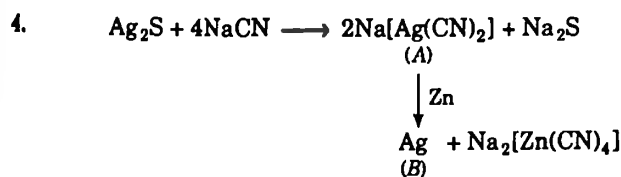
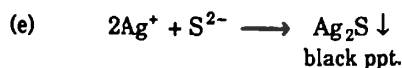
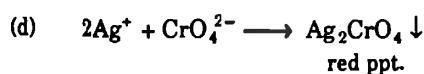
- $\text{AgNO}_3$  is soluble in excess of hypo. Give reaction.
- $\text{AgNO}_3$  solution can be used to identify following radicals by the colour of the ppt obtained :
  - $\text{Cl}^-$
  - $\text{Br}^-$
  - $\text{I}^-$
  - $\text{CrO}_4^{2-}$
  - $\text{S}^{2-}$
 Specify the colour of the precipitate
- Unreacted  $\text{AgBr}$  in photography is removed by hypo used as 'fixer'. What is the reaction ?
- $\text{Ag}_2\text{S} \xrightarrow{\text{aq NaCN}} (\text{A}) \xrightarrow{\text{Zn}} (\text{B})$   
Identify (A) and (B).
- Give the scheme of extraction of silver from silver coins.
- How is  $\text{AgNO}_3$  determined volumetrically?
- (a) When  $\text{H}_2\text{S}$  gas is passed into  $\text{FeCl}_3$  solution, yellow colour of  $\text{FeCl}_3$  changes to light green. Explain  
(b) Same behaviour is also observed when  $\text{SnCl}_2$  solution is added. Explain.
- $\text{K}_3[\text{Fe}(\text{CN})_6]$ , potassium ferricyanide, is used as external indicator in the volumetric estimation of  $\text{Fe}^{2+}$  salts by  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$  solution. How does it indicate end-point?
- Aqueous  $\text{FeCl}_3$  forms acidic solution due to hydrolysis and there is evidence of  $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  ion. This forms dimer at pH 4 – 5. What is structure of dimer ?
- Identify (A) to (F) in the following:  

$$\text{FeSO}_4 (\text{A}) \xrightarrow{\Delta} (\text{B}) + (\text{C}) + (\text{D})$$
 (C) and (D) are gases, (B) is red-brown solid, (C) can be oxidised to (D). (C) also turns  $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$  solution green. (B) dissolves in  $\text{HCl}$  forming deep yellow solution (E). (E) gives blue colour (F) with  $\text{K}_4[\text{Fe}(\text{CN})_6]$ . (D) dissolves in  $\text{H}_2\text{O}$  forming a well known mineral acid called "king of acids".
- In earlier days  $\text{Fe}_2\text{O}_3$  was used to prepare  $\text{NaOH}$  in which  $\text{Fe}_2\text{O}_3$  was recycled. Give scheme of this method.
- Complete
  - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} + \text{NaOCl} \longrightarrow$
  - $\text{Fe}_2\text{O}_3 + \text{LiOH} \xrightarrow{\Delta}$
  - $\text{Fe}_2\text{O}_3 + \text{H}_2\text{C}_2\text{O}_4 \longrightarrow$   
(rust)
  - $\text{Fe}_2\text{O}_3 + \text{CO} \xrightarrow{\Delta}$
  - $\text{Fe}_2\text{O}_3 + \text{H}_2 \xrightarrow{\Delta}$
- What happens when :
  - $\text{Fe}_2(\text{SO}_4)_3$  reacts with  $\text{Fe}$ .
  - $\text{FeCO}_3$  reacts with dil  $\text{H}_2\text{SO}_4$ .
  - $\text{FeSO}_4$  reacts with  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$  and then  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is added.
  - $\text{FeSO}_4$  is strongly heated.
- $\text{FeSO}_4$  can be determined volumetrically by titration with  $\text{K}_2\text{Cr}_2\text{O}_7$  using  $\text{K}_3[\text{Fe}(\text{CN})_6]$  as an external indicator. What is the end-point ?
- 2.78 g of  $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$  is treated with excess of  $\text{BaCl}_2$  when 2.33 g of white ppt are obtained. Calculate the value of  $x$ . ( $\text{Ba} = 137$ ,  $\text{S} = 32$ ,  $\text{Fe} = 56$ ,  $\text{H} = 1$ ,  $\text{O} = 16$ )
- Give chemical tests for making distinction between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions.
- Aqueous  $\text{FeSO}_4$  gives test for  $\text{Fe}^{2+}$  and  $\text{SO}_4^{2-}$  but after excess of  $\text{KCN}$  is added, solution does not give test for  $\text{Fe}^{2+}$ . Explain.
- Copper (II) ion in basic solution is reduced by formaldehyde,  $\text{HCHO}$  to copper (I) oxide. Formaldehyde is oxidised to formate,  $\text{HCOO}^-$ . Write the balanced equations for this reaction.
- You are supposed to be 'pathologist' in a medical lab. You are given a sample of urine of a diabetic patient. How will you detect the presence of sugar in it ?
- A blue coloured mixture is supposed to contain  $\text{Cd}^{2+}$  ion also along with  $\text{Cu}^{2+}$  ion. How is the presence of  $\text{Cd}^{2+}$  detected ?
- $\text{Cu}^{2+}$  ion gives deep violet colour with glycine  $\text{CH}_2(\text{NH}_2)\text{COOH}$ . Give its equation.  
(For more problem refer Practice Exercise 4)

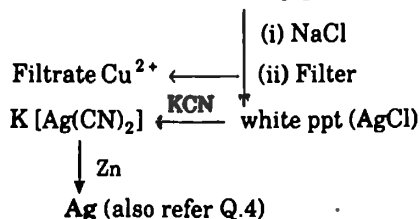
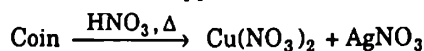
## Answers

- $$2\text{AgNO}_3 + \text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \underset{\text{white ppt.}}{\text{Ag}_2\text{S}_2\text{O}_3} + 2\text{NaNO}_3$$

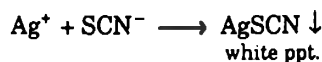
$$\text{Ag}_2\text{S}_2\text{O}_3 + 3\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \underset{\text{sodium argento thiosulphate (soluble)}}{2\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]}$$
- (a) 
$$\text{Ag}^+ + \text{Cl}^- \longrightarrow \underset{\text{white ppt. soluble in } \text{NH}_3 (\text{aq})}{\text{AgCl} \downarrow}$$
- (b) 
$$\text{Ag}^+ + \text{Br}^- \longrightarrow \underset{\text{yellow ppt. partially soluble in } \text{NH}_3 (\text{aq})}{\text{AgBr} \downarrow}$$
- (c) 
$$\text{Ag}^+ + \text{I}^- \longrightarrow \underset{\text{yellow ppt. insoluble in } \text{NH}_3 (\text{aq})}{\text{AgI} \downarrow}$$



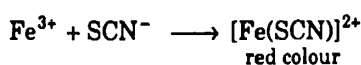
5. Silver coin has silver and copper metals (in the form of alloy).



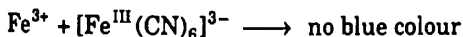
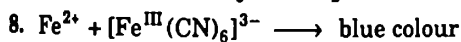
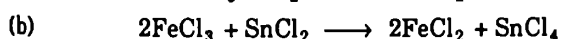
6. AgNO<sub>3</sub> can be determined volumetrically by titration using NH<sub>4</sub>SCN (ammonium sulphocyanide) with ferric alum as indicator:



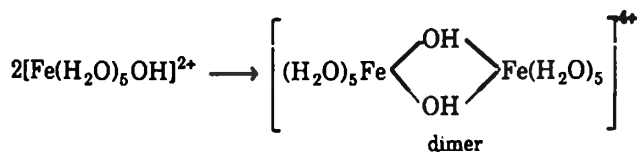
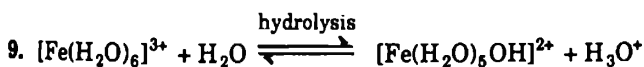
When precipitation is complete, additional drop of SCN<sup>-</sup> gives red colour with Fe<sup>3+</sup> of ferric alum:



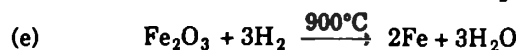
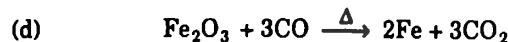
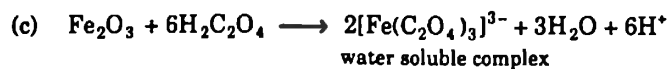
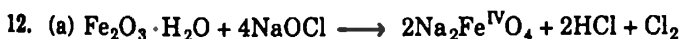
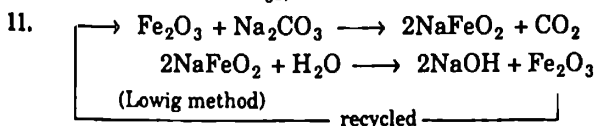
7. In both cases Fe<sup>2+</sup> ions are formed due to reduction. Hence, solution appears light green:



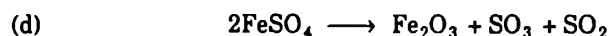
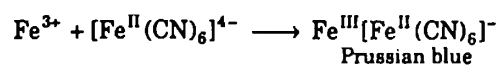
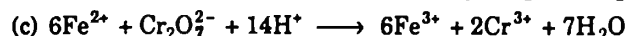
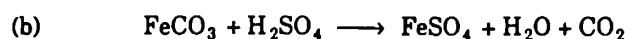
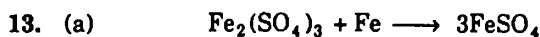
Initially when Fe<sup>2+</sup> is present, indicator K<sub>3</sub>[Fe(CN)<sub>6</sub>] gives blue colour. After Fe<sup>2+</sup> is completely oxidised to Fe<sup>3+</sup>, there is no colour with indicator.



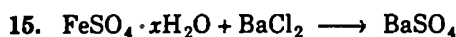
10. (A) : FeSO<sub>4</sub> (B) : Fe<sub>2</sub>O<sub>3</sub> (C) : SO<sub>2</sub> (D) : SO<sub>3</sub> (E) : FeCl<sub>3</sub>  
(F) : KFe<sup>III</sup>[Fe<sup>II</sup>(CN)<sub>6</sub>], Prussian blue



Reaction 12(c) has wide application in removing iron rust stains (Fe<sub>2</sub>O<sub>3</sub>) from fabric. If oxalic acid is used, then Fe(+III) forms complex [Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> which can be washed with water.



14. Fe<sup>2+</sup> salts give blue colour with K<sub>3</sub>[Fe<sup>III</sup>(CN)<sub>6</sub>] being used as an external indicator. After Fe<sup>2+</sup> has been completely oxidised to Fe<sup>3+</sup>, there is no colour change when tested with K<sub>3</sub>[Fe(CN)<sub>6</sub>].



$$152 + 18x$$

$$233$$

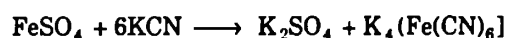
$$2.78$$

$$2.33$$

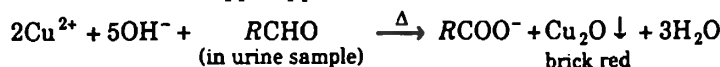
$$\Rightarrow \quad x = 7$$

| 16. Reagent                           | Fe <sup>2+</sup>               | Fe <sup>3+</sup>           |
|---------------------------------------|--------------------------------|----------------------------|
| NaOH                                  | green ppt                      | red-brown ppt              |
| K <sub>4</sub> [Fe(CN) <sub>6</sub> ] | white ppt turning blue rapidly | Prussian blue ppt          |
| K <sub>3</sub> [Fe(CN) <sub>6</sub> ] | Turnbull's blue ppt            | red brown colour (no ppt.) |
| KSCN                                  | no colour                      | deep red colour            |

17. It is due to formation of the complex K<sub>4</sub>[Fe(CN)<sub>6</sub>] in which CN<sup>-</sup> has been coordinated to Fe<sup>2+</sup>



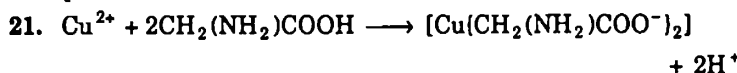
19. Urine sample of the diabetic patient is supposed to contain glucose. Hence, when it is heated with Fehling's solution, (see text) a brick red ppt. appears.



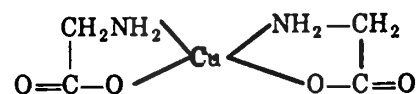
20. If KCN in excess is added to the mixture, Cu<sup>2+</sup> forms a stable complex [Cu<sup>I</sup>(CN)<sub>4</sub>]<sup>3-</sup> while Cd<sup>2+</sup> forms unstable complex [Cd(CN)<sub>4</sub>]<sup>2-</sup>. This complex ionises :



When H<sub>2</sub>S gas is passed, yellow ppt. of CdS appears if Cd<sup>2+</sup> is present.



or



## Inner-Transition Elements (*f*-Block)

As we have specified earlier, the elements with a partially filled *f*-subshell in common oxidation states are known as ***f*-block transition elements** or **inner-transition elements**. They are the **two rows** elements at the bottom of the Periodic Table. (*4f* and *5f*-series).

- Fourteen elements of the first row (*4f*-series) from cerium ( $Z = 58$ ) to lutetium ( $Z = 71$ ) which follow lanthanum ( $Z = 57$ ) in the Periodic Table are called **Lanthanides** or **Lanthanoids** or **Lanthanones**. These elements are characterised by successive filling of *4f*-orbitals in their atoms. Lanthanides along with yttrium ( $Z = 39$ ) and lanthanum ( $Z = 57$ ) were originally called as rare earths since their oxides (earths) were rare.

Fourteen elements of the second row (*5f*-series) from thorium ( $Z = 90$ ) to lawrencium ( $Z = 103$ ) following actinium are known as **Actinides** or **Actinoids** or **Actinones**. These are characterised by successive filling of *5f*-orbital. Actinides from  $Z = 93$  (after uranium  $Z = 92$ ) have been produced artificially and are known as **transuranium elements**.

## The Lanthanoids

### Electronic Configuration

- Shells  $n$ ,  $(n - 1)$  and  $(n - 2)$  are incomplete and  $(n - 2)f$ , i.e., *4f*-orbital is being successively filled.
- Lanthanum ( $Z = 57$ ) has electronic configuration  $[\text{Xe}]5d^1 6s^2$ .
- There is an electron in *5d*-orbital only in Ce ( $Z = 58$ ) Gd ( $Z = 64$ ) and in Lu ( $Z = 71$ ). This is just to explain extra stability of half-filled or completely filled *4f*-orbitals.
- Lanthanides mostly from ionic compounds in +3 oxidation state, the electronic configuration of  $M^{3+}$  ions from  $Z = 58$  to  $Z = 71$  varies in a regular manner from  $[\text{Xe}]4f^1$  to  $[\text{Xe}]4f^{14}$ . Electronic configuration have been summarised in Table 16.10.

## Atomic and Ionic Sizes :

### (The Lanthanide Contraction)

The observed values of the atomic radii and ionic radii of the trivalent lanthanide ion ( $\text{Ln}^{3+}$ ) have been summarised in Table 16.10. Like the ions of the transition elements, the ionic radii show a progressive decrease with increasing atomic number. The decrease in size of  $\text{Ln}^{3+}$  ion in *4f*-series is known as **lanthanide contraction**. (Fig. 16.7)

- In lanthanides, electrons in *4f*-orbitals are being filled progressively. Since addition of an extra electron in *4f* (screening constant of  $(n - 2)f$  electron = 1)

orbital exactly balances the additional unit of nuclear charge, and thus effective nuclear charge ( $Z_{\text{eff}}$ ) remains unchanged. Hence, it would be predicted that the atomic radii should also remain constant. Table 16.10. shows that there is slight decrease in the value of atomic radius along the series (with exception that of Eu and Yb. These two metals crystallise with cubic lattices and attain oxidation state of +2. It is to be noted that the *4f*-orbitals are half-filled ( $4f^7$ ) and completely filled ( $4f^{14}$ ).

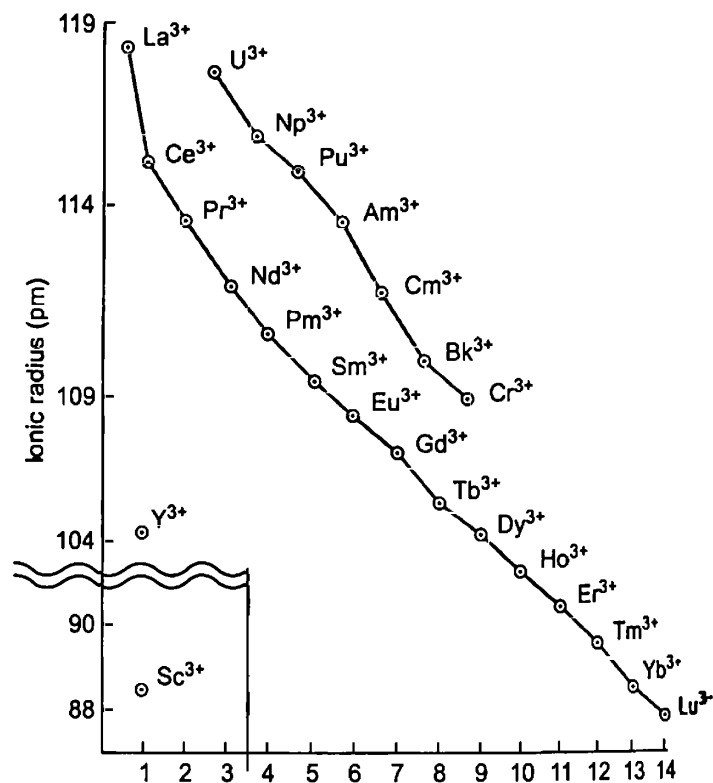


Fig. 16.7 Ionic radii (CN = 6) of  $\text{Sc}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Ln}^{3+}$  and  $\text{An}^{3+}$  ions

When the trivalent ion  $\text{Ln}^{3+}$  is formed, then screening power of *4f*-electron is no longer equal to unity (but 0.85 since *4f* is now  $[(n - 1), \text{penultimate shell}]$ , and each time an electron is added to *4f*-orbitals, the effective nuclear charge ( $Z_{\text{eff}}$ ) is increased by 0.15 and thus ionic size ( $r_n \propto \frac{1}{Z_{\text{eff}}}$ ) of  $\text{Ln}^{3+}$  decreases continuously from  $\text{Ce}^{3+}$  to  $\text{Lu}^{3+}$ .

## DEEP Focus

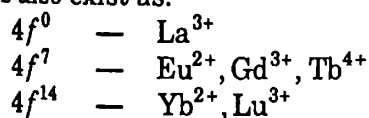
- As a result of lanthanide contraction, the normal increase in size from  $\text{Sc} \rightarrow \text{Y} \rightarrow \text{La}$  disappears after the lanthanide and the pairs of elements such as **Zr and Hf**, **Nb and Ta**, **Mo and W**, etc. have nearly same size. The properties of these elements are very similar.
- The similarities in properties within these pairs make their separation very difficult.
- Due to lanthanide contraction, the elements of *5d* and *4d*-transition series resemble each other much more closely than do the elements of *4d* and *3d* series.

Table 16.10 Electronic Configuration and Other Physical Constants of Lanthanum and Lanthanides

| Name         | Atomic number | Symbol | Oxidation state | Electronic configuration outside [Xe] Core |                  |                  |                  | Radius/pm |                  | $E^\circ/V$<br>$M^{3+}/M$ | $I_1 + I_2 + I_3$<br>$\text{kJ mol}^{-1}$ |
|--------------|---------------|--------|-----------------|--------------------------------------------|------------------|------------------|------------------|-----------|------------------|---------------------------|-------------------------------------------|
|              |               |        |                 | Ln                                         | Ln <sup>2+</sup> | Ln <sup>3+</sup> | Ln <sup>4+</sup> | Ln        | Ln <sup>3+</sup> |                           |                                           |
| Lanthanum    | 57            | La     | III             | $5d^1 6s^2$                                | $5d^1$           | $4f^0$           |                  | 187       | 106              | -2.52                     | 3455                                      |
| Cerium       | 58            | Ce     | III, IV         | $4f^1 5d^1 6s^2$                           | $4f^2$           | $4f^1$           | $4f^0$           | 183       | 103              | -2.48                     | 3524                                      |
| Praseodymium | 59            | Pr     | III (IV)        | $4f^3 6s^2$                                | $4f^3$           | $4f^2$           | $4f^1$           | 182       | 101              | -2.46                     | 3631                                      |
| Neodymium    | 60            | Nd     | III             | $4f^4 6s^2$                                | $4f^4$           | $4f^3$           | $4f^2$           | 181       | 100              | -2.43                     | 3692                                      |
| Promethium   | 61            | Pm     | III             | $4f^5 6s^2$                                | $4f^5$           | $4f^4$           |                  | 181       | 98               | -2.42                     | 3728                                      |
| Samarium     | 62            | Sm     | III(II)         | $4f^6 6s^2$                                | $4f^6$           | $4f^5$           |                  | 179       | 96               | -2.41                     | 3871                                      |
| Europium     | 63            | Eu     | III(II)         | $4f^7 6s^2$                                | $4f^7$           | $4f^6$           |                  | 204       | 95               | -2.41                     | 4057                                      |
| Gadolinium   | 64            | Gd     | III             | $4f^7 5d^1 6s^2$                           | $4f^7 5d^1$      | $4f^7$           |                  | 180       | 94               | -2.40                     | 3763                                      |
| Terbium      | 65            | Tb     | III(IV)         | $4f^9 6s^2$                                | $4f^9$           | $4f^8$           | $4f^7$           | 178       | 92               | -2.39                     | 3798                                      |
| Dysprosium   | 66            | Dy     | III(IV)         | $4f^{10} 6s^2$                             | $4f^{10}$        | $4f^9$           | $4f^8$           | 177       | 91               | -2.35                     | 3918                                      |
| Holmium      | 67            | Ho     | III             | $4f^{11} 6s^2$                             | $4f^{11}$        | $4f^{10}$        |                  | 176       | 89               | -2.32                     | 3920                                      |
| Erbium       | 68            | Er     | III             | $4f^{12} 6s^2$                             | $4f^{12}$        | $4f^{11}$        |                  | 175       | 88               | -2.30                     | 3930                                      |
| Thulium      | 69            | Tm     | III(II)         | $4f^{13} 6s^2$                             | $4f^{13}$        | $4f^{12}$        |                  | 174       | 87               | -2.28                     | 4044                                      |
| Ytterbium    | 70            | Yb     | III(II)         | $4f^{14} 6s^2$                             | $4f^{14}$        | $4f^{13}$        |                  | 194       | 86               | -2.27                     | 4193                                      |
| Lutetium     | 71            | Lu     | III             | $4f^{14} 5d^1 6s^2$                        | $4f^{14} 5d^1$   | $4f^{14}$        |                  | 174       | 85               | -2.26                     | 3887                                      |

## Oxidation States

The sum of the first three ionisation energies of the lanthanides is comparatively low, so the elements are highly electropositive. They readily form Ln<sup>3+</sup> ions by losing both the 6s and one 5d-electrons. In the absence of 5d electron, one of the electrons present in the (n-2)f orbitals is lost. Besides the +3 state, some of the lanthanides show other oxidation states. Following stable ions also exist as:



Stability of these ions depend on

- ionisation energy
- sublimation energy
- lattice energy.

## Colour of Ions

Ions of lanthanides are coloured in the solid state as well as in aqueous solution (except La<sup>3+</sup>, Ce<sup>3+</sup>, Gd<sup>3+</sup>, Yb<sup>3+</sup> and Lu<sup>3+</sup>). Colour of these ions arise due to electronic transition in 4f-orbitals (f – f\*). Colours of Ln<sup>3+</sup> ions have been summarised in Table 16.11.

## Magnetic Properties

Paramagnetism is associated with the presence of unpaired electrons in a substance. Ln<sup>3+</sup> ions other than f<sup>0</sup> type (La<sup>3+</sup> and Ce<sup>4+</sup>) and the f<sup>14</sup> type (Yb<sup>2+</sup> and Lu<sup>3+</sup>) are all paramagnetic. The values of magnetic moment have been given in Table 16.11



Table 16.11 The Colours and Observed and Calculated Magnetic Moment of  $\text{La}^{3+}$  and  $\text{Ln}^{3+}$  Ions

| Ion              | Colour<br>(aquo complex) | Electronic<br>configuration | $N$<br>(unpaired electrons) | Magnetic moment of $N$ unpaired<br>electrons/ $\mu$ BM |           |
|------------------|--------------------------|-----------------------------|-----------------------------|--------------------------------------------------------|-----------|
|                  |                          |                             |                             | Calculated<br>(only total spin)                        | Observed  |
|                  |                          |                             |                             | $\sqrt{N(N+2)}$                                        |           |
| $\text{La}^{3+}$ | colourless               | $4f^0$                      | 0                           | 0.0                                                    | 0         |
| $\text{Ce}^{3+}$ | colourless               | $4f^1$                      | 1                           | 1.73                                                   | 2.3–2.5   |
| $\text{Pr}^{3+}$ | green                    | $4f^2$                      | 2                           | 2.83                                                   | 3.4–3.6   |
| $\text{Nd}^{3+}$ | lilac                    | $4f^3$                      | 3                           | 3.87                                                   | 3.5–3.6   |
| $\text{Pm}^{3+}$ | yellow                   | $4f^4$                      | 4                           | 4.90                                                   | 2.70      |
| $\text{Sm}^{3+}$ | yellow                   | $4f^5$                      | 5                           | 5.92                                                   | 1.5–1.6   |
| $\text{Eu}^{3+}$ | pale pink                | $4f^6$                      | 6                           | 6.93                                                   | 3.4–3.6   |
| $\text{Gd}^{3+}$ | colourless               | $4f^7$                      | 7                           | 7.94                                                   | 7.8–8.0   |
| $\text{Tb}^{3+}$ | pale pink                | $4f^8$                      | 6                           | 6.93                                                   | 9.4–9.6   |
| $\text{Dy}^{3+}$ | yellow                   | $4f^9$                      | 5                           | 5.92                                                   | 10.4–10.5 |
| $\text{Ho}^{3+}$ | pale yellow              | $4f^{10}$                   | 4                           | 4.90                                                   | 10.3–10.5 |
| $\text{Er}^{3+}$ | rose-red (pink)          | $4f^{11}$                   | 3                           | 3.87                                                   | 9.4–9.6   |
| $\text{Tm}^{3+}$ | pale-green               | $4f^{12}$                   | 2                           | 2.83                                                   | 7.1–7.4   |
| $\text{Yb}^{3+}$ | colourless               | $4f^{13}$                   | 1                           | 1.73                                                   | 4.4–4.9   |
| $\text{Lu}^{3+}$ | colourless               | $4f^{14}$                   | 0                           | 0.00                                                   | 0         |

Colours of  $\text{Ln}^{4+}$ ,  $\text{Ln}^{2+}$  ions are given below

$\text{Ce}^{4+}$  — orange-red  $4f^0$  isoelectronic of  $\text{La}^{3+}$

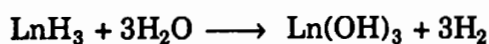
$\text{Sm}^{2+}$  — blood-red  $4f^6$  isoelectronic of  $\text{Eu}^{3+}$

$\text{Eu}^{2+}$  — pale greenish yellow  $4f^7$  isoelectronic of  $\text{Gd}^{3+}$

$\text{Yb}^{2+}$  — yellow  $4f^{14}$  isoelectronic of  $\text{Lu}^{3+}$

## Chemical Reactivity

- The lanthanide elements (as well as La and Y) are all silvery white, soft and malleable with high electrical conductivity. Eu and Yb are pale yellow.
- They are highly electropositive and reactive. All of them burn in air to form oxides  $\text{Ln}_2\text{O}_3$  and nitrides  $\text{LnN}$  (cerium gives  $\text{CeO}_2$ ). Powdered cerium is even pyrophoric. Yttrium usually forms a protective oxide coating on it and remains unattacked by air even at 1273 K.
- The hydrides, formed in stable in  $\text{H}_2$  and  $\text{LnH}_3$  phases, usually have a defect lattice and are non-stoichiometric. They react with  $\text{H}_2\text{O}$  liberating  $\text{H}_2$  gas.



The hydrides are remarkable stable to heat up to 1200 K

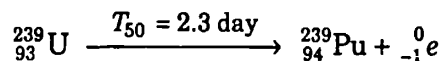
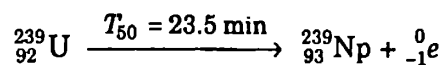
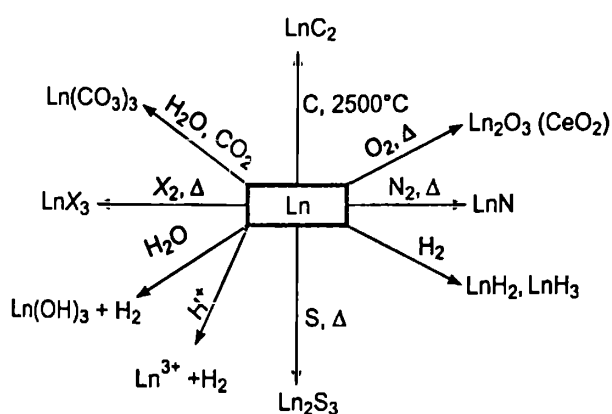
- They form trihalides with halogens but Ce and Tb give  $\text{CeF}_4$  and  $\text{TbF}_4$  respectively. Complex fluorides of Pr(IV), Nd(IV) and Dy(IV) are also formed.

- The hydroxides are ionic and basic. They are less basic than  $\text{Ca}(\text{OH})_2$  but more basic than amphoteric  $\text{Al}(\text{OH})_3$ . The base strength decreases from  $\text{Ce}(\text{OH})_3$  to  $\text{Lu}(\text{OH})_3$ .
- Non-availability of  $d$ -electrons for  $\pi$ -bonding does not favour the formation of carbonyls by most lanthanides. However, an unstable  $\text{Nd}(\text{CO})_6$  has been prepared.
- Since  $E^\circ$  for  $\text{Ln}^{3+} + 3e^- \longrightarrow \text{Ln}$  is negative, they react directly with water, rapidly on heating, to liberate  $\text{H}_2$ . Reactions with acids are more vigorous, but the metals do not dissolve in alkalis. They are also stable in  $\text{HF}$  and  $\text{H}_3\text{PO}_4$  owing to the formation of a protective film of insoluble salts.

## DEEP Focus

Europium and ytterbium dissolve in liquid ammonia at 195 K forming blue solutions which give spectra characteristic of  $M^{2+}$  and ammoniated electrons. The solution decolourises slowly but the concentrated solution appear golden.

- An alloy of lanthanide metal is **mischmetal**. It has lanthanide metal (95%) and iron about 5% with traces of S, C, Ca and Al and is used in the production of bullets, shells and lighter flint. Mixed oxides of lanthanides are used as catalysts in petroleum cracking. Oxides are also used as **phosphorus** in television screens.



- At present, transuranium elements with atomic number upto 110 have been reported. Recently, on August 16, 2003, IUPAC approved the name for the element with atomic number 110 as DARMSTADIUM (Ds)

The IUPAC proposed a system for naming elements with  $Z > 100$ .

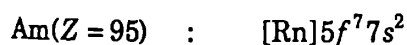
| Digits | Name | Abbreviation |
|--------|------|--------------|
| 0      | nil  | n            |
| 1      | un   | u            |
| 2      | bi   | b            |
| 3      | tri  | t            |
| 4      | quad | q            |
| 5      | pent | p            |
| 6      | hex  | h            |
| 7      | sept | s            |
| 8      | oct  | o            |
| 9      | enn  | e            |

## The Actinoids

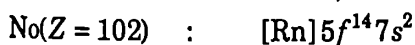
The actinoids are the fourteen elements from Th to Lr following actinium in the seventh period of the Periodic Table. They are radioactive, and therefore of the greatest importance in the study of nuclear chemistry and of the principles which underline the conversion of mass into energy.

## Electronic Configuration

Three shells ( $n$ ,  $(n-1)$  and  $(n-2)$ ) are incompletely filled and differentiating electron enters into  $5f$ -orbital [i.e.,  $(n-2)f$ ]. Electronic configurations (EC) of actinoids and their ions have been given in Table 17.13. The variation in the (EC) of the actinoids like those in lanthanoids is due to extra stabilities of  $f^0$ ,  $f^7$  and  $f^{14}$  EC of the  $5f$ -orbitals. Thus, EC of Am and Cm are with  $5f^7$  arrangements.



Similarly Th( $Z = 90$ ) has  $5f^0$  and No ( $Z = 102$ ) and Lr( $Z = 103$ ) have  $5f^{14}$  arrangements



## DEEP Focus

The allocation of electrons to the  $5f$  or  $6d$ -orbitals in the actinide atoms is more uncertain than the allocation to the  $4f$  or  $5d$ -orbitals in the lanthanide atoms, because the external shielding of the  $5f$ -electrons is less than that of the  $4f$ -electrons.

## Transuranic Elements

Elements with atomic numbers greater than 92 (atomic number of uranium) are called the transuranium elements. All these elements are man-made, i.e., they are produced in the laboratory through artificial nuclear reactions.

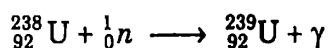


Table 16.12 IUPAC Nomenclature of Elements with Atomic Number above 100

| Atomic number | Name           | Symbol | IUPAC official name | IUPAC symbol |
|---------------|----------------|--------|---------------------|--------------|
| 101           | Un-nil-unium   | Unu    | Mendelevium         | Md           |
| 102           | Un-nil-bium    | Unb    | Nobelium            | No           |
| 103           | Un-nil-trium   | Unt    | Lawrencium          | Lr           |
| 104           | Un-nil-quadium | Unq    | Rutherfordium       | Rf           |
| 105           | Un-nil-pentium | Unp    | Dubnium             | Db           |
| 106           | Un-nil-hexium  | Unh    | Seaborgium          | Sg           |
| 107           | Un-nil-septium | Uns    | Bohrium             | Bh           |
| 108           | Un-nil-octium  | Uno    | Hassium             | Hs           |
| 109           | Un-nil-ennium  | Une    | Meitnerium          | Mt           |
| 110           | Un-un-illium   | Unn    | Darmstadtium***     | Ds           |
| 111           | Un-un-unium    | Uuu    | **                  |              |
| 112           | Un-un-bium     | Uub    | **                  |              |
| 113           | Un-un-trium    | Uut    | *                   |              |
| 114           | Un-un-quadium  | Uuq    | **                  |              |
| 115           | Un-un-pentium  | Uup    | *                   |              |
| 116           | Un-un-hexium   | Uuh    | *                   |              |
| 117           | Un-un-septium  | Uus    | *                   |              |
| 118           | Un-un-octium   | Uuo    | *                   |              |

\*Elements yet to be discovered,

\*\*IUPAC names yet to be announced.

\*\*\*IUPAC approved the name on August 16, 2003.

[illegible]

## Magnetic Properties

The magnetic properties of the actinoids is again dependent on unpaired electrons ( $N$ ) and are given by

$$\mu \text{ (magnetic moment)} = \sqrt{N(N+2)} \text{ BM}$$

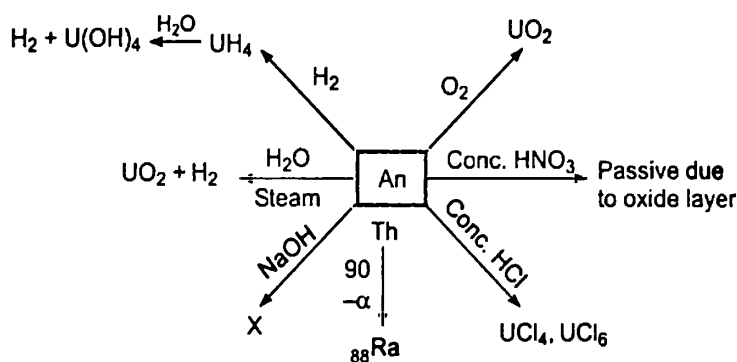
but observed values are more complex than those of lanthanoids and have been summarised in Table 16.15.

Table 16.15 Magnetic Moment of Actinoids

| Element | Z   | N | $\mu = \sqrt{N(N+2)} \text{ BM (only total spin)}$ |
|---------|-----|---|----------------------------------------------------|
| Th      | 90  | 2 | 2.83                                               |
| Pa      | 91  | 3 | 3.87                                               |
| U       | 92  | 4 | 4.90                                               |
| Np      | 93  | 5 | 5.92                                               |
| Pu      | 94  | 6 | 6.93                                               |
| Am      | 95  | 7 | 7.94                                               |
| Cm      | 96  | 8 | 8.94                                               |
| Bk      | 97  | 5 | 5.92                                               |
| Cf      | 98  | 4 | 4.90                                               |
| Es      | 99  | 3 | 3.87                                               |
| Fm      | 100 | 2 | 2.83                                               |
| Md      | 101 | 1 | 1.73                                               |
| No      | 102 | 0 | 0.00                                               |
| Lr      | 103 | 1 | 1.73                                               |

## Physical and Chemical Properties

- The actinoids metals are all silvery in appearance with a variety of structure.
- The dominant feature of the actinoids is their nuclear instability as they have tendency to undergo spontaneous fission and decay becomes more pronounced with the heavier elements. The radioactivity of Th and U is probably responsible for much of the earth's internal heat.
- The actinoids metals are more electropositive and are reactive, reactivity increase with increase in atomic number.
- They tarnish rapidly in air, forming an oxide coating which is protective in case of Th but less for the other elements.
- The metals react with most non-metals especially on heating, but resist alkali attack and are less reactive towards acids than might be expected. Concentrated HCl react rapidly but concentrated  $\text{HNO}_3$  makes Th, U and Pu passive, which can be prevented in presence of  $\text{F}^-$ .
- With boiling water or steam,  $\text{H}_2$  is obtained and metal is converted into oxide.
- Metals react rapidly with  $\text{H}_2$  forming hydrides which are decomposed by  $\text{H}_2\text{O}$ .



## Ionisation Energy

- Ionisation energy of the early actinoids are smaller than those of early lanthanoids. When electrons are being filled into  $5f$ -orbitals they will penetrate less into the inner core of the electrons and thus these occupied  $5f$ -electrons will be more effectively shielded from the nuclear charge than are the  $4f$ -electrons of the corresponding lanthanoids.

## Target Practice 4

**Note:** This also includes problems from  $d$ -block elements.

- Write formulae of
  - Calomel .....
  - Corrosive sublimate .....
  - Nessler's reagent .....
  - Iodide of Millon's base .....
- Mercury (I) chloride is written as  $\text{Hg}_2\text{Cl}_2$  and not as  $\text{HgCl}$  because .....
- A magician showed following performances in a magic show. But you immediately disclosed their secrets by chemical reactions.
  - He rubbed a white substance on a copper coin which was covered with a silvery layer. It is due to .....

- He took two colourless solutions. On adding one into another dropwise, orange precipitate appeared which dissolved on adding excess of that. It was explained as .....
- He placed some white substance with 10 paise coin on the palm of a child and asked to close it tightly. After sometime, palm got hot and child cried. It was due to .....

- $\text{TiO}_2$  can be converted into  $\text{TiCl}_4$  and *vice-versa*. Explain based on reactions .....

5. What are the contents of the Ziegler-Natta catalyst?

6. Select species which are amphoteric or amphiprotic?

| Species                         | Amphoteric | Amphiprotic |
|---------------------------------|------------|-------------|
| I : $\text{TiO}_2$              |            |             |
| II : $\text{H}_2\text{O}$       |            |             |
| III : $\text{Al}_2\text{O}_3$   |            |             |
| IV : $\text{ZnO}$               |            |             |
| V : $\text{HSO}_4^-$            |            |             |
| VI : $\text{H}_2\text{PO}_2^-$  |            |             |
| VII : $\text{H}_2\text{PO}_3^-$ |            |             |
| VIII : $\text{HPO}_4^{2-}$      |            |             |

7. What are the contents of mischmetal?

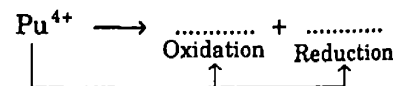
8. Mention ion of following electronic configuration in valence shell

- (a)  $4f^0$  .....  
 (b)  $4f^7$  .....  
 (c)  $4f^{14}$  .....

9. Lanthanides does not form carbonyl because .....  
 What happens when europium or ytterbium is dissolved in liquid ammonia?

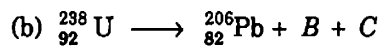
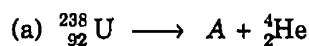
10. Write maximum oxidation states of the following  
 (a) U ..... (b) Np ..... (c) Bk .....

11. (a) In acidic solution  $\text{Pu}^{4+}$  disproportionates. Write chemical reaction



(b)  $\text{UO}_2^{2+}$  disproportionates to ..... and .....

12. Balance following nuclear reactions



13. Write IUPAC symbol for the elements with atomic number

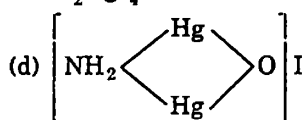
- (a) 100 ..... (d) 112 .....  
 (b) 101 ..... (e) 114 .....  
 (c) 110 .....

## Answers

1. (a)  $\text{Hg}_2\text{Cl}_2$

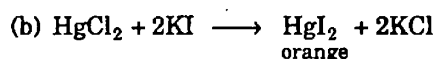
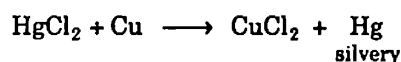
(b)  $\text{HgCl}_2$

(c)  $\text{K}_2\text{HgI}_4$

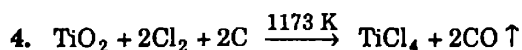
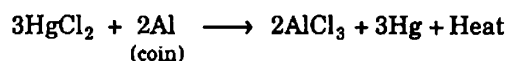


2. Mercurous ions is diamagnetic indicating the absence of any unpaired electrons. Hence, mercurous ion is not  $\text{Hg}^+$  but  $\text{Hg}_2^{2+}$ .

3. (a) Formation of Hg layer by reduction of  $\text{HgCl}_2$  to Hg by copper.



(c) Exothermic reaction



5. Triethyl aluminium and titanium (IV) chloride.

| Species                       | Amphoteric | Amphiprotic |
|-------------------------------|------------|-------------|
| I $\text{TiO}_2$              | ✓          | X           |
| II $\text{H}_2\text{O}$       | X          | ✓           |
| III $\text{Al}_2\text{O}_3$   | ✓          | X           |
| IV $\text{ZnO}$               | ✓          | X           |
| V $\text{HSO}_4^-$            | ✓          | ✓           |
| VI $\text{H}_2\text{PO}_2^-$  | X          | X           |
| VII $\text{H}_2\text{PO}_3^-$ | ✓          | ✓           |
| VIII $\text{HPO}_4^{2-}$      | ✓          | ✓           |

7. 95% lanthanide, 5% iron with traces of sulphur, carbon, calcium and aluminium.

8. (a)  $4f^0$  :  $\text{La}^{3+}$

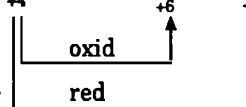
(b)  $4f^7$  :  $\text{Eu}^{2+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Tb}^{4+}$

(c)  $4f^{14}$  :  $\text{Yb}^{2+}$ ,  $\text{Lu}^{2+}$

9. of non-availability of d-electrons for  $\pi$ -bonding.

10. (a) U = +6 (b) Np = +7 (c) Bk = +4

11. (a)  $\text{Pu}^{4+} \longrightarrow \text{PuO}_2^{2+} + \text{Pu}^{3+}$



(b)  $\text{U}^{4+}$  and  $\text{UO}_2^{2+}$

12. (a) A :  ${}_{90}^{234}\text{Th}$  (b) B :  $8\alpha$  C :  $6\beta$

13. (a) Unn (b) Unu (c) Uun (d) Uub (e) Uuq

## Practice Exercise 4

- Mercurous ion has zero magnetic moment. It is represented as  $\text{Hg}^+$ ,  $\text{Hg}_2^{2+}$  or  $\text{Hg}_2^+$ , explain.
- What is van't Hoff factor of  $\text{Hg}_2(\text{NO}_3)_2$  if it is 100% ionised in aqueous solution?
- Give the scheme of separation of mixture of insoluble  $\text{AgCl}$ ,  $\text{Hg}_2\text{Cl}_2$  and  $\text{PbCl}_2$ .
- When  $\text{K}_2\text{HgI}_4$  reacts with  $\text{NH}_3$ , brown ppt is formed. Explain the formation of brown ppt
- Make distinction between  $\text{Hg}_2^{2+}$  and  $\text{Hg}^{2+}$  salts.
- (a) What happens when a solution of  $\text{HgCl}_2$  is boiled with a solution of  $\text{HgO}$ ?  
(b) What happens when  $\text{HgCl}_2$  is dissolved in conc.  $\text{HCl}$ ?
- Ilmenite ( $\text{FeTiO}_3$ ) can also be converted into  $\text{TiCl}_4$  by heating with carbon and chlorine. Write a balanced equation for this reaction.
- $\text{TiCl}_4$  can be converted to pure Ti by reduction with Na or Mg. Write chemical equation.
- Explain lanthanide contraction
- Write EC of (a) Gd, (b)  $\text{Gd}^{3+}$  (c)  $\text{Lu}^{3+}$   
Also determine magnetic moment (assuming total spin only).
- Compare base strength of  $\text{Ln}(\text{OH})_3$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$
- Compare lanthanoids and actinoids in terms of:  
(a) EC (b) ionic size  
(c) radioactivity (d) oxidation state
- Complete the following reactions:  
(a)  $\text{Pu}^{4+} \xrightarrow{\text{H}^+}$  (b)  $\text{UO}_2^{2+} \xrightarrow{\text{H}^+}$   
(c)  $\text{U}^{4+} \xrightarrow{\text{H}_2\text{O}/\text{O}_2}$

## Answers

- $\text{Hg}^{2+}$  has no electron unpaired hence, its magnetic moment is zero, but it is called mercuric [ $\text{Hg}(\text{II})$ ] ion.  $\text{Hg}^+$  has one unpaired electron, it has magnetic moment of  $\sqrt{3}$  BM, but mercurous ion has zero magnetic moment, it is only possible if it has all paired electrons. Thus it is  $\text{Hg}_2^{2+}$ .



$$\text{Total ions} = y = 3$$

$$i (\text{van't Hoff factor}) = (1 + (y - 1)x)$$

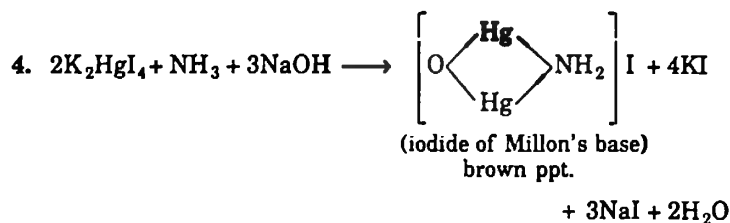
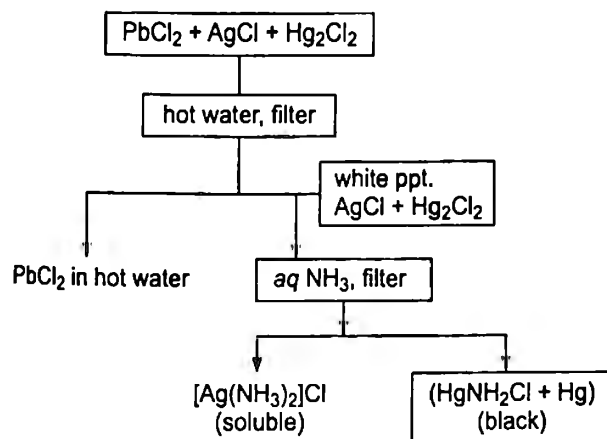
$$= 1 + 2x \quad (x = \text{degree of ionisation} = 1)$$

$$= 1 + 2 = 3$$

- (a)  $\text{PbCl}_2$  is soluble in hot water;  $\text{Hg}_2\text{Cl}_2$  and  $\text{AgCl}$  are insoluble in hot water.

(b)  $\text{AgCl}$  is soluble in aq  $\text{NH}_3$ .

(c)  $\text{Hg}_2\text{Cl}_2$  is blackened by aq  $\text{NH}_3$

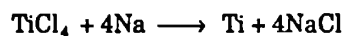


| 5. Reagent                 | $\text{Hg}_2^{2+}$                         | $\text{Hg}^{2+}$                                                         |
|----------------------------|--------------------------------------------|--------------------------------------------------------------------------|
| • KI                       | green ppt. which dissolves in excess of KI | orange ppt. which dissolves in excess of KI ( $\text{K}_2\text{HgI}_4$ ) |
| • HCl                      | white ppt ( $\text{Hg}_2\text{Cl}_2$ )     | no ppt.                                                                  |
| • $\text{H}_2\text{S}$ gas | no ppt.                                    | black ppt ( $\text{HgS}$ ).                                              |

- (a) Mercury oxychlorides are formed:



(b)  $\text{H}_2\text{HgCl}_4$  is formed which crystallises on cooling.



9. Refer text      10. Refer text

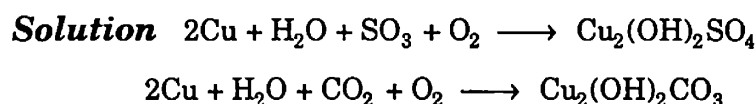
11. Refer text      12. Refer text

13. Refer text

# Total Practice Set

## (Read, Plan & Solve!)

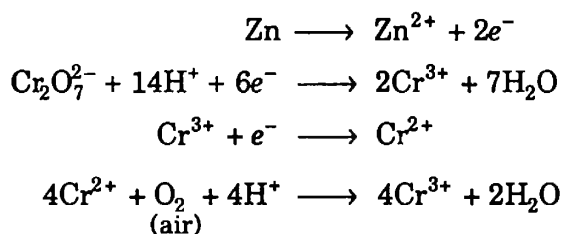
**Problem 1.** In an atmosphere with industrial smog, Cu corrodes to a basic sulphate  $\text{Cu}_2(\text{OH})_2\text{SO}_4$  and basic carbonate  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ . Propose a series of chemical reactions to describe this corrosion.



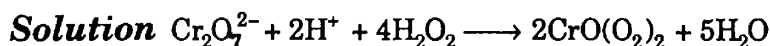
Fortunately this corrosion product forms a tough adherent coating that protects the underlying metal. Overall reaction is a combination of oxidation-reduction, acid-base and precipitation reaction.

**Problem 2.** When Zn is added to an acidified solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ , the colour of the solution changes from orange to green, then to blue and over a period of time, back to green. Write equations for this series of reactions.

**Solution** Zn reduces  $\text{Cr}_2\text{O}_7^{2-}$  (orange)/ $\text{H}^+$  to  $\text{Cr}^{3+}$  (green) and then to  $\text{Cr}^{2+}$  (blue), but atmospheric  $\text{O}_2$  oxidises  $\text{Cr}^{2+}$  (blue) back to  $\text{Cr}^{3+}$  (green):



**Problem 3.** In qualitative analysis, a confirmatory test for chromium involves the formation of a blue transient peroxo species,  $\text{CrO}_5$ , which is better represented as  $\text{CrO}(\text{O}_2)_2$ . It is formed when  $\text{H}_2\text{O}_2$  is added to an acidic solution containing  $\text{Cr}_2\text{O}_7^{2-}$ . What is oxidation state of Cr in  $\text{CrO}(\text{O}_2)_2$ ? Write the equation of formation of  $\text{CrO}_5$ .



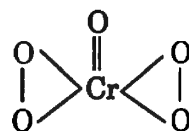
Oxidation state of oxygen in peroxide = -1

Oxidation state of oxygen in oxide = -2

Hence, in  $\text{CrO}(\text{O}_2)_2$  ← four oxygen of peroxide.

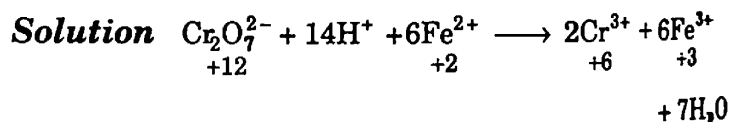
$$\begin{array}{c} \uparrow \quad \uparrow \quad \uparrow \\ x - 2 - 4 = 0 \end{array}$$

$$x = +6$$



**Problem 4.** Both  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{MnO}_4^-$  solutions can be used to titrate  $\text{Fe}^{2+}$  in acidic medium.

Suppose you have available 0.1 M solutions of each. For a given sample of  $\text{Fe}^{2+}$  solution, if a given titration requires 24.5 mL of 0.1 M  $\text{Cr}_2\text{O}_7^{2-}$  solution, how many mL of 0.1 M  $\text{MnO}_4^-$  solution would have been required if it had been used instead?



$\text{Cr}_2\text{O}_7^{2-} \equiv 6e^-$  ] gain of  $6e^-$  by two Cr atoms.

$$\therefore 0.1\text{M } \text{Cr}_2\text{O}_7^{2-} = 0.6\text{ N } \text{Cr}_2\text{O}_7^{2-}$$



$$\text{MnO}_4^- \equiv 5e^-$$

$$\therefore 0.1\text{M } \text{MnO}_4^- \equiv 0.5\text{ N } \text{MnO}_4^-$$

$$\text{Fe}^{2+} \equiv \text{Cr}_2\text{O}_7^{2-} \equiv \text{MnO}_4^-$$

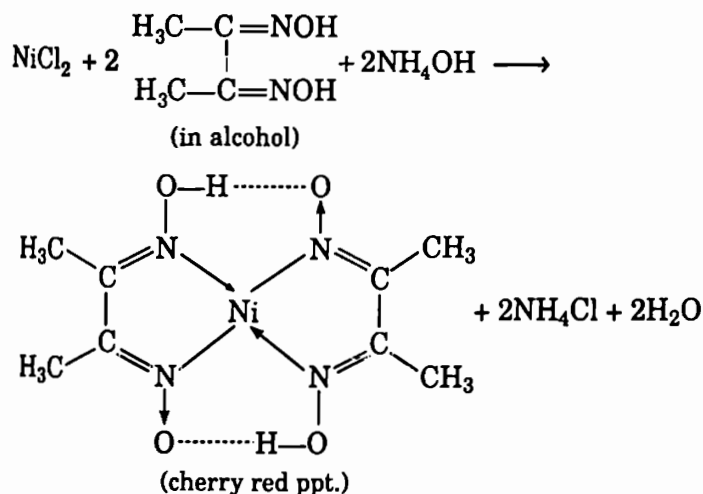
$$24.5\text{ mL of } 0.1\text{M } \text{Cr}_2\text{O}_7^{2-} \equiv V\text{ mL of } 0.1\text{M } \text{MnO}_4^-$$

$$24.5\text{ mL} \times 0.6\text{ N } \text{Cr}_2\text{O}_7^{2-} \equiv V\text{ mL of } 0.5\text{ N } \text{MnO}_4^-$$

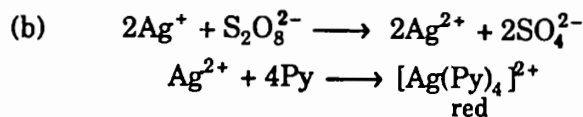
$$V = \frac{24.5 \times 0.6}{0.5} = 29.4\text{ mL}$$

**Problem 5.** Nickel can be determined by the precipitation of nickel dimethyl glyoximate. What is the reaction?

**Solution** (a)  $\text{Ni}^{2+}$  salts (in basic medium) on reaction with dimethyl glyoxime give cherry red ppt of nickel dimethyl glyoximate:



The extreme toxicity of cyanides is due to  $\text{CN}^-$  complexing with metals in cytochrome-enzymes and haemoglobin in the body, thus preventing normal metabolism.

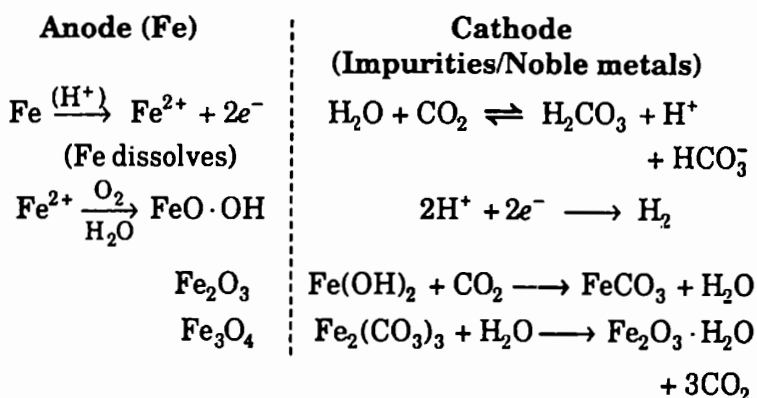


**Problem 8.** Explain the terms:

- (a) Rusting, (b) Passivity.

**Solution** (a) **Rusting** : When exposed to air and moisture, iron gets rapidly oxidised to a hydrated oxide,  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ , known as rust of iron. Actual composition is not known, but it consists mainly of  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  together with a small quantity of  $\text{FeCO}_3$ .

Rusting is an electrochemical phenomenon. When impure iron comes in contact with water containing  $\text{CO}_2$ , an internal voltaic cell is set up. The iron and the other metals present as impurities constitute the electrode while aerated water (having  $\text{CO}_2$ ) acts as an electrolyte. As iron is more electropositive than many other metals, it passes into solution as iron (II) ion more readily than the rest of the metals.



Iron is protected from rusting by:

- galvanisation (by a coating of Zn)
- electroplating with Ni or Cr
- heating the iron to redness in steam when a protective coating of  $\text{Fe}_3\text{O}_4$  (ferrosoferric oxide) is formed – Barf Process.
- painting with  $\text{Pb}_3\text{O}_4$ ,  $\text{PbCrO}_4$ ,  $\text{ZnCrO}_4$  etc.

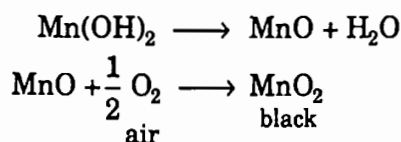
(b) **Passivity** : When a piece of iron is dipped in conc.  $\text{HNO}_3$ , a slight reaction takes place which then ceases completely. There is no change in the appearance of the iron, but this does not displace Cu from  $\text{CuSO}_4$  solution which is however a common property of Fe. This behaviour is also observed with Cr and Al when in contact with  $\text{HNO}_3$ . These metals in this form are said to be **passive**.

Passive iron returns to normal state when scratched or heated in a reducing atmosphere of  $\text{H}_2$  or CO or immersed in a conc. alkaline solution.

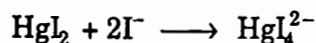
**Problem 6.** (a) When  $\text{Mn}(\text{OH})_2$  is made by adding an alkali to a solution containing  $\text{Mn}^{2+}$  ions, the precipitate quickly darkens, and eventually goes black. What might be the chemical giving the black colour, and how is it made?

(b) Dimercury (I) iodide,  $\text{Hg}_2\text{I}_2$  is a greenish colour and is precipitated if iodide ions are added to a solution of dimercury (I) sulphate,  $\text{Hg}_2\text{SO}_4$ . Likewise the red mercury (II) iodide,  $\text{HgI}_2$ , is precipitated from a solution of mercury (II) sulphate,  $\text{HgSO}_4$ . However, both precipitates dissolve in excess iodide solution. What might be the reason for this?

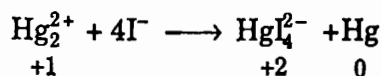
**Solution** (a) The black colour is due to the manganese (IV) oxide,  $\text{MnO}_2$ . It is made by the  $\text{Mn}(\text{OH})_2$  being oxidised by oxygen in the air:



(b) It is due to formation of  $\text{HgI}_4^{2-}$  (a soluble complex) in both the cases with  $\text{HgI}_2$  :



But in  $\text{Hg}_2\text{I}_2$ , first there is oxidation of Hg(I) to Hg(II) and then complex formation takes place; it is by following disproportionation reaction :



**Problem 7.** (a) CO and  $\text{CN}^-$  are toxic. Explain by a suitable example.

(b)  $\text{S}_2\text{O}_8^{2-}$  (peroxy disulphate ion) oxidises  $\text{Ag}^+$  in the presence of excess pyridine. Write chemical reaction.

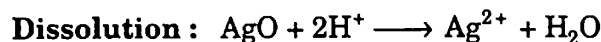
**Solution** (a) CO is toxic because it forms a complex with iron of haemoglobin in the blood, and this complex is more stable than oxy-haemoglobin. This prevents the haemoglobin in the red blood corpuscles from carrying oxygen round the body. This causes an oxygen deficiency, leading to unconsciousness and then death.



Passivity of iron is believed to be due to the formation of an extremely thin layer of  $\text{Fe}_3\text{O}_4$  on the surface. **Passivity of iron prevents it from rusting.**

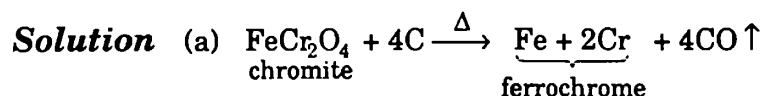
**Problem 9.** In acidic solution silver (II) oxide first dissolves to produce  $\text{Ag}^{2+}$ . This is followed by oxidation of  $\text{H}_2\text{O}$  to  $\text{O}_2$  and the reduction of  $\text{Ag}^{2+}$  to  $\text{Ag}^+$ . Write chemical equations for the dissolution and redox reactions.

### Solution

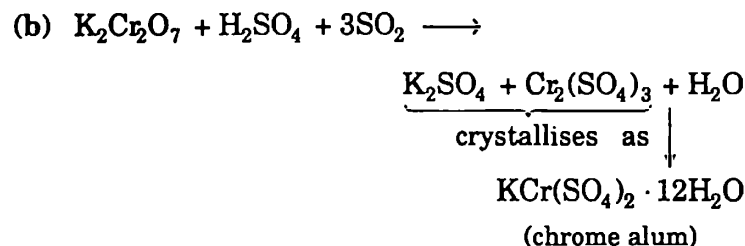


**Problem 10.** How are the following prepared?

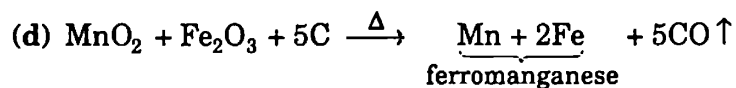
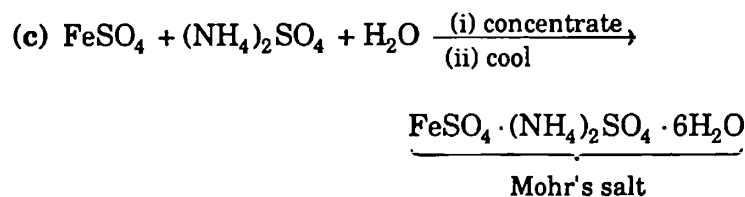
- (a) Ferrochrome      (b) Chrome alum  
(c) Mohr's salt      (d) Ferromanganese



Ferrochrome is an alloy (of Fe and Cr) and can be added directly to iron, together with other metals, to produce steel.



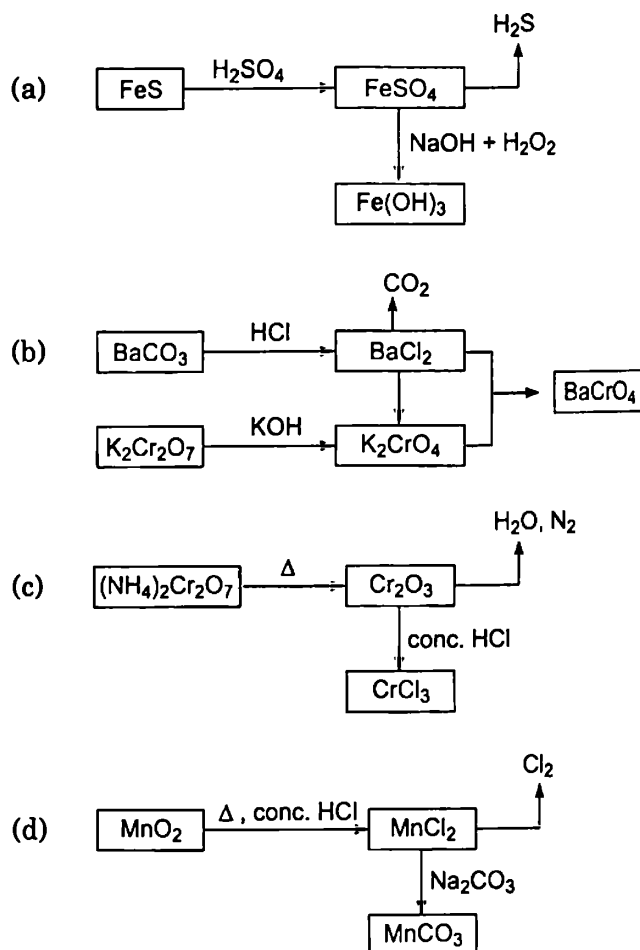
It is used in tanning hides, dyeing textiles and fixing baths in photography.



**Problem 11.** Suggest a series of reactions, using common chemicals, by which each of the following syntheses can be performed?

- (a)  $\text{Fe}(\text{OH})_3$  from  $\text{FeS}$   
 (b)  $\text{BaCrO}_4$  from  $\text{BaCO}_3$  and  $\text{K}_2\text{Cr}_2\text{O}_7$   
 (c)  $\text{CrCl}_3$  from  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$   
 (d)  $\text{MnCO}_3$  from  $\text{MnO}_2$

### Solution



**Problem 12.** Write chemical reactions for the following :

- (a)  $\text{Mn}^{3+}$  disproportionates to  $\text{Mn}^{2+}$  and  $\text{MnO}_2$  in acidic medium  
 (b)  $\text{MnO}_4^{2-}$  disproportionates to  $\text{MnO}_2$  and  $\text{MnO}_4^-$  in acidic medium  
 (c)  $\text{MnO}_4^{2-}$  is obtained if  $\text{MnO}_2$  reacts with  $\text{MnO}_4^-$  in basic medium.  
 (d) Zn reduces  $\text{VO}^{2+}$  to  $\text{V}^{3+}$  in acidic medium

### Solution

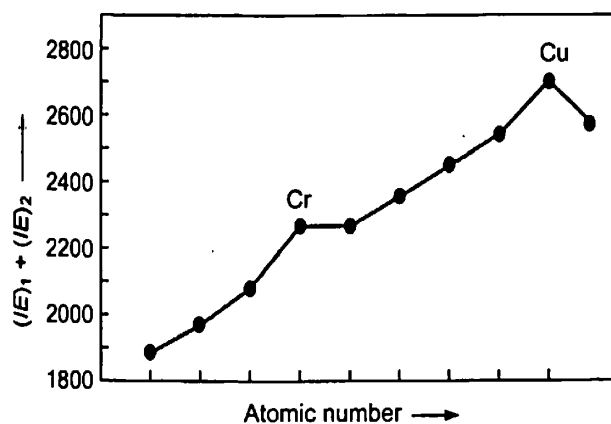
- (a)  $2\text{Mn}^{3+} + \text{H}_2\text{O} \longrightarrow \text{Mn}^{2+} + \text{MnO}_2 + 4\text{H}^+$   
 (b)  $3\text{MnO}_4^{2-} + 4\text{H}^+ \longrightarrow \text{MnO}_2 + 2\text{MnO}_4^- + 2\text{H}_2\text{O}$   
 (c)  $\text{MnO}_2 + 2\text{MnO}_4^- + 4\text{OH}^- \longrightarrow 3\text{MnO}_4^{2-} + 2\text{H}_2\text{O}$   
 (d)  $\text{Zn} + 2\text{VO}^{2+} + 4\text{H}^+ \longrightarrow \text{Zn}^{2+} + 2\text{V}^{3+} + 2\text{H}_2\text{O}$

**Problem 13.** Calculate the sum of the first two ionisation energies for the first-series transition elements, from Table 16.1 and account for the general trend.

**Solution** (From Table 16.1)

| Element | Z  | (IE) <sub>1</sub> | (IE) <sub>2</sub> | (IE) <sub>2</sub> + (IE) <sub>1</sub> |
|---------|----|-------------------|-------------------|---------------------------------------|
| Sc      | 21 | 631               | 1235              | 1866                                  |
| Ti      | 22 | 656               | 1309              | 1965                                  |
| V       | 23 | 650               | 1413              | 2063                                  |
| Cr      | 24 | 652               | 1591              | 2243                                  |
| Mn      | 25 | 717               | 1509              | 2226                                  |
| Fe      | 26 | 762               | 1561              | 2323                                  |
| Co      | 27 | 758               | 1645              | 2403                                  |
| Ni      | 28 | 736               | 1751              | 2487                                  |
| Cu      | 29 | 775               | 1958              | 2733                                  |
| Zn      | 30 | 906               | 1733              | 2639                                  |

Across the first transition element series,  $Z_{\text{eff}}$  increases and there is an almost linear increase in the sum of first two ionisation energies. This is what is expected if the two electrons are removed from the 4s-orbital. Higher than the expected values for the sum of first two ionisation energies are observed for Cr and Cu, because of their anomalous electron configurations (Cr:  $3d^5 4s^1$  and Cu:  $3d^{10} 4s^1$ ). An increasing  $Z_{\text{eff}}$  affects 3d-orbitals more than the 4s-orbital and the second ionisation energy for an electron from the 3d-orbital is higher than expected.



**Problem 14.** A solution may contain any of the following ions:  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ . The solution is treated as outlined below, with the results indicated. Which of the ions is (are) probably present? Are there some ions about which you have insufficient information to reach a decision? Explain.

- The original unknown solution is treated with  $(\text{NH}_4)_2\text{S}(\text{aq})$  in a buffered basic solution. A dark precipitate is obtained.
- With the exception of a small residue of sulphur, the precipitate from (1) is completely soluble in aqua-regia ( $\text{HNO}_3 + \text{HCl}$ )

- The solution from (2) is treated with  $\text{NaOH}(\text{aq})$  and  $\text{H}_2\text{O}_2(\text{aq})$ . A dark precipitate separates from the solution. The solution is colourless.
- The precipitate from (3) dissolves in dil.  $\text{HCl}$  to produce a coloured solution.
- The solution from (4) is treated with  $\text{NH}_3(\text{aq})$ . A dark precipitate forms.
- The precipitate from (5) is soluble in  $\text{HCl}(\text{aq})$  and the solution develops an intense red colour when treated with  $\text{SCN}^-(\text{aq})$ .

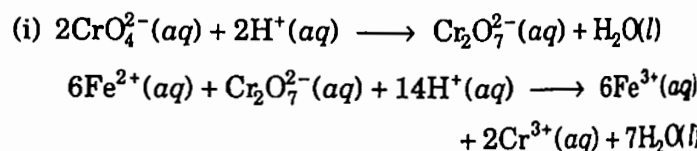
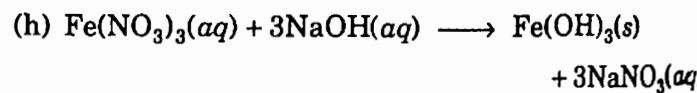
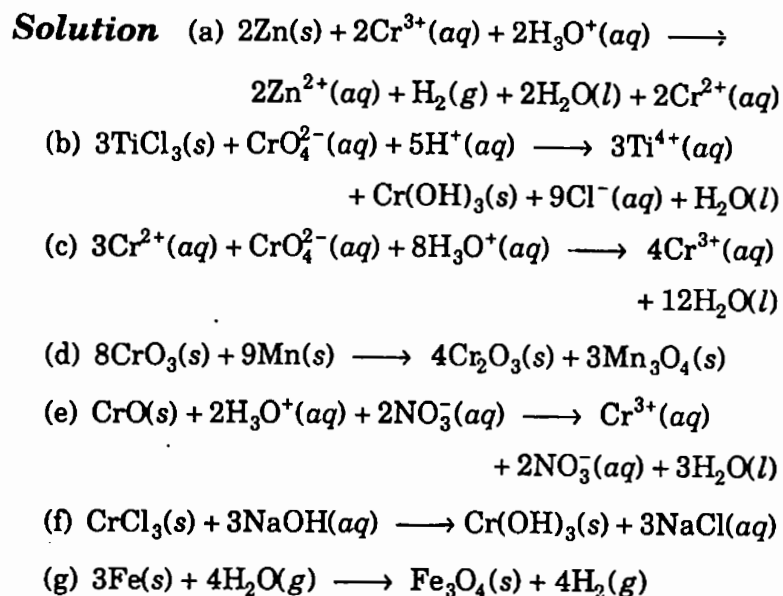
**Solution**

| Scheme                                                                                    | Conclusion                                                                                                                                                                                                                                                                                 |
|-------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| (1) and (2)                                                                               | A dark precipitate may be due to $\text{NiS}$ , $\text{Cr}_2\text{S}_3$ , $\text{Fe}_2\text{S}_3$ , $\text{MnS}$ . ( $\text{ZnS}$ is colourless)                                                                                                                                           |
| (3)                                                                                       | $\text{Cr}^{3+}$ is not possible since this treatment makes $\text{Cr}^{3+}$ as $\text{Na}_2\text{CrO}_4$ soluble. Possibility of $\text{Ni}^{2+}$ and $\text{Mn}^{2+}$ is rejected since solution (in upper layer) is colourless. A dark precipitate is due to $\text{Fe}(\text{OH})_3$ . |
| (4)                                                                                       | $\text{Fe}(\text{OH})_3$ is soluble in dil. $\text{HCl}$ forming $\text{FeCl}_3$ (coloured)                                                                                                                                                                                                |
| (5)                                                                                       | $\text{FeCl}_3$ is precipitated as $\text{Fe}(\text{OH})_3$ on addition of $\text{NH}_3(\text{aq})$ .                                                                                                                                                                                      |
| (6)                                                                                       | $\text{Fe}(\text{OH})_3$ is again soluble in dil. $\text{HCl}$ , and $\text{FeCl}_3$ formed gives intense red colour with $\text{SCN}^-$                                                                                                                                                   |
| $\text{Fe}^{3+} + \text{SCN}^- \longrightarrow [\text{Fe}(\text{SCN})]^{2+}_{\text{red}}$ |                                                                                                                                                                                                                                                                                            |

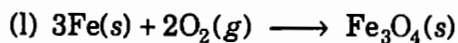
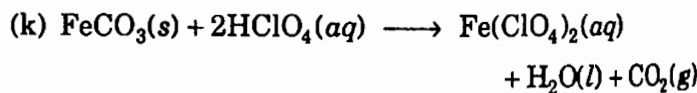
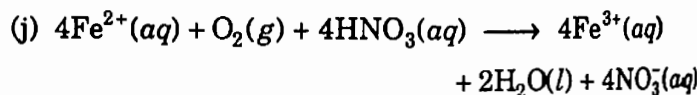
|                  |                                                          |
|------------------|----------------------------------------------------------|
| Probably present | : $\text{Fe}^{3+}$                                       |
| Probably absent  | : $\text{Cr}^{3+}$                                       |
| Uncertain        | : $\text{Ni}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Mn}^{2+}$ |

**Problem 15.** Predict the products of the following reactions :

- Zn is added to a solution of  $\text{Cr}_2(\text{SO}_4)_3$  in acid.
- $\text{TiCl}_3$  is added to a solution containing an excess of  $\text{CrO}_4^{2-}$  ion.
- $\text{Cr}^{2+}$  is added to  $\text{CrO}_4^{2-}$  in acid solution.
- Mn is heated with  $\text{CrO}_3$
- $\text{CrO}$  is added to  $\text{HNO}_3$  solution
- $\text{CrCl}_3$  is added to  $\text{NaOH}$  solution
- Fe is heated in an atmosphere of steam
- $\text{NaOH}$  is added to solution of  $\text{Fe}(\text{NO}_3)_3$
- $\text{Fe}(\text{NO}_3)_2$  is added to an acidic solution of  $\text{K}_2\text{CrO}_4$
- A solution of  $\text{Fe}(\text{NO}_3)_2$  and  $\text{HNO}_3$  is allowed to stand in air
- $\text{FeCO}_3$  is added to a solution of  $\text{HClO}_4$
- Fe is heated in air.



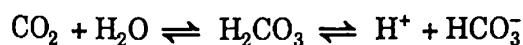
(In presence of  $\text{H}^+$ ,  $\text{CrO}_4^{2-}$  changes to  $\text{Cr}_2\text{O}_7^{2-}$  which oxidises  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ )



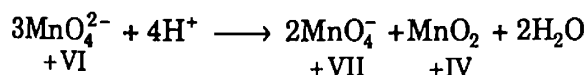
### Explanation

- (a) ***Explain why a green solution of potassium manganate (VI)  $K_2MnO_4$  turns purple and a brown solid is precipitated when  $CO_2$  is bubbled into the solution.***

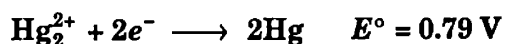
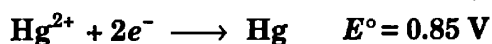
- $\text{CO}_2$  in aqueous solution is acidic



In presence of  $H^+$ ,  $MnO_4^{2-}$  disproportionates to  $MnO_4^-$  (purple, by oxidation) and  $MnO_2$  (brown solid, by reduction)

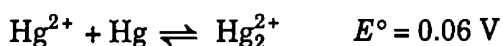


- (b) *When mercury is oxidised with a limited amount of oxidising agent (i.e., an excess of  $\text{Hg}$ ) then  $\text{Hg}^{\text{I}}$  compounds are formed. If there is an excess of oxidising agent, then  $\text{Hg}^{\text{II}}$  compounds are formed.*

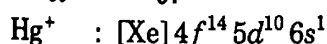
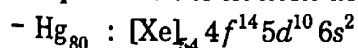


- The standard reduction potentials are so close that oxidising agents like  $\text{HNO}_3$  will convert  $\text{Hg}$  to  $\text{Hg}_2^{2+}$  rather than  $\text{Hg(I)}$  if the oxidising agent is present in excess.

The reduction potential diagram shows that  $\text{Hg}_2^{2+}$  is stable to disproportionation by a small margin under standard conditions :



- (c) *The mercurous ion is written as  $\text{Hg}_2^{2+}$  while the cuprous ion is written as  $\text{Cu}^+$ .*



In  $\text{Hg}^{\text{I}}$ , there is one unpaired electron and we expect  $\text{Hg}^{\text{I}}$  (mercurous) salt to be paramagnetic. But magnetic moment of mercurous salt is zero indicating that it is diamagnetic which is only possible when 6s electron has been used by two Hg atoms in bonding. Hence, mercurous ion is  $\text{Hg}_2^{2+}$ .



$\text{Cu}^{\text{I}}$  (cuprous) salt is diamagnetic by experiment and thus it is not dimeric and is thus  $\text{Cu}^+$ .

- (d) ZnO is yellow when hot, but white when cold.**

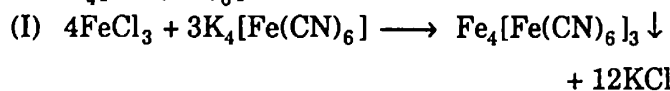
- $\text{Zn}^{2+}$  has  $3d^{10}$  EC hence all electrons paired thus form white salt. The yellow colour of hot ZnO is due to defects in the solid structure which increases with temperature.

- (e)  $\text{Cu}^+$  is a  $d^{10}$  ion and colourless but  $\text{Cu}_2\text{O}$  is red and  $\text{Cu}_2\text{S}$  is black.

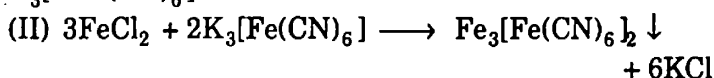
- $\text{Cu}^+$  is a  $d^{10}$  ion so that there is no  $d-d^*$  transition and thus the ion is colourless. But  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{S}$  are coloured because of charge transfer of electrons from  $\text{O}^{2-}$  or  $\text{S}^{2-}$  to the vacant orbital of  $\text{Cu}^+$ .

- (f) *Prussian blue and Turnbull's blue have different chemical formula, yet they are identical.*

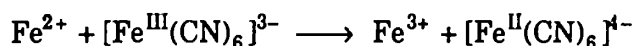
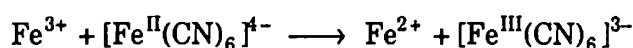
- Prussian blue is formed as an intense blue precipitate when a solution of ferric salt is treated with  $K_4[Fe^{II}(CN)_6]$ .



Turnbull's blue is formed as a deep blue precipitate when a solution of ferrous salt is treated with  $\text{K}_3[\text{Fe}^{\text{III}}(\text{CN})_6]$ .



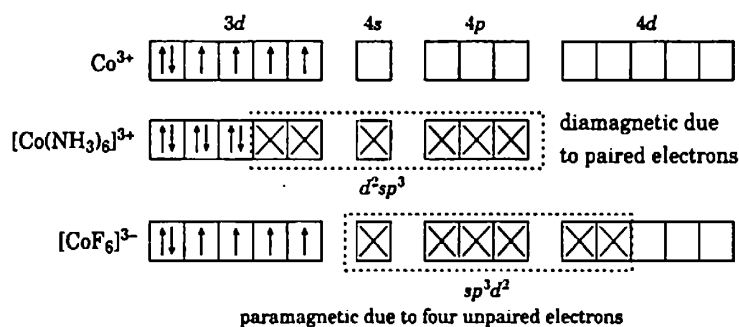
X-ray studies have established that Prussian blue and Turnbull's blue are identical. When either of the reactions (I) and (II) is performed, a redox reaction also takes place partially :



Thus, both of these compounds have a mixture of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$

hence we write Prussian blue and Turnbull's blue as  $\text{Fe}[\text{Fe}(\text{CN})_6]^-$  that can be due to  $\text{Fe}^{2+}$  and  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$  shown as  $\text{Fe}^{\text{II}}(\text{Fe}^{\text{III}}(\text{CN})_6)$  or due to  $\text{Fe}^{3+}$  and  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$  shown as  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$ .

- (g)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is diamagnetic and  $[\text{CoF}_6]^{3-}$  is strongly paramagnetic.



$\text{Co}^{3+}$  has  $3d^6$ -configuration with four unpaired electrons in ground state. In presence of  $\text{NH}_3$  (strong ligand) all the unpaired electrons in  $\text{Co}^{3+}$  get **paired** and thus  $[\text{Co}(\text{NH}_3)_6]^{3+}$  has  $d^2sp^3$  hybridisation (octahedral structure), thus it is diamagnetic (no electron unpaired).  $\text{F}^-$  is a weak ligand hence, six lone

pairs of six  $F^-$  are filled in outer  $d$ -orbitals of  $Co^{3+}$  which has now four electrons unpaired. Thus  $CoF_6^{3-}$  has  $sp^3d^2$  hybridisation in  $Co^{3+}$  and is thus paramagnetic due to unpaired electrons.

(h) **For the first row transition metal the  $E^\circ$  values are**

| $E^\circ$    | V     | Cr    | Mn    | Fe    | Co    | Ni    | Cu    |
|--------------|-------|-------|-------|-------|-------|-------|-------|
| $(M^{2+}/M)$ | -1.18 | -0.91 | -1.18 | -0.44 | -0.28 | -0.25 | +0.34 |

Explain the irregularity in the above values.

The  $E^\circ(M^{2+}/M)$  values are not regular which can be explained from the irregular variation of ionization energies ( $IE_1 + IE_2$ ) and also the sublimation energies which are relatively much less for manganese and vanadium. (240  $\text{kJ mol}^{-1}$  for manganese and 470  $\text{kJ mol}^{-1}$  for vanadium).

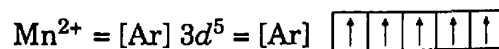
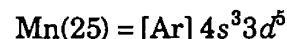
(i) **Explain as to why the  $E^\circ$  value for the  $Mn^{3+}/Mn^{2+}$  couple is much more positive than that for  $Cr^{3+}/Cr^{2+}$  or  $Fe^{3+}/Fe^{2+}$ .**

- Much larger third ionization energy to Mn (where the required change is  $d^5$  to  $d^4$ ) is mainly responsible for

this. This also explains why the +3 state of Mn is of little importance.

(j) **Although  $Mn^{2+}$  ion has five unpaired electrons,  $[Mn(H_2O)_6]^{2+}$  is not intensely coloured.**

- Spin multiplicity is defined as  $= (2s + 1)$  where,  $s$  = sum of spin.



Thus, 
$$s = 5 \times \frac{1}{2} = \frac{5}{2}$$

Hence, multiplicity  $= (2s + 1) = 6$

Multiplicity of excited state can't be six.

Thus, electronic transition in  $Mn^{2+}$  are spin forbidden, hence  $[Mn(H_2O)_6]^{2+}$  salts appear colourless.

Also,  $[Mn(H_2O)_6]^{2+}$  has centre of symmetry and in such cases electronic transitions are expected to be Laporte forbidden.

# Master Exercises

## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

- How many ions are obtained in the following complexes due to ionisation in aqueous solution ?  
(a)  $\text{PtCl}_4 \cdot 6\text{H}_2\text{O}$  (b)  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$   
(c)  $\text{CrCl}_3 \cdot 5\text{H}_2\text{O}$  (d)  $\text{CuCl}_2 \cdot 4\text{NH}_3$
- Calculate magnetic moments of  $M^{2+}$  ions (divalent cations) of 3d-series and arrange them in the increasing order.
- Magnetic moment of  $[\text{Fe}(\text{CN})_6]^{4-}$  is zero but that of  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  is  $\sqrt{24}$  BM Explain.
- Arrange  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$  in increasing order of magnetic moment.
- Magnetic of  $\text{Fe}^{3+}$  ion is  $\sqrt{35}$  BM. Determine number of unpaired electrons. Also write its electronic configuration.
- s- and p-block elements form colourless ions. Explain.
- Which of the following ions are coloured/colourless ?  
(a)  $\text{Zn}^{2+}$  (b)  $\text{Cu}^+$   
(c)  $\text{Cu}^{2+}$  (d)  $\text{Sc}^{3+}$   
(e)  $\text{Ti}^{2+}$  (f)  $\text{V}^{3+}$   
(g)  $\text{Mn}^{2+}$  (h)  $\text{Ni}^{2+}$   
(i)  $\text{Na}^+$  (j)  $\text{Ca}^{2+}$
- Assuming Aufbau rule is not known then which of the following ions would be coloured?  
(a)  $\text{K}^+$  (b)  $\text{Cu}^+$   
(c)  $\text{Ca}^+$  (d)  $\text{Sc}^{2+}$
- $\text{Hg}^{2+}$  salts are colourless. Explain.
- Which of the following are paramagnetic, coloured, and coloured and paramagnetic both?  
 $\text{NO}_2$ ,  $\text{Cu}^+$ ,  $\text{O}_2$ ,  $\text{O}_3$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Cd}^{2+}$ , Al, C (graphite)
- Compounds, containing the  $\text{Sc}^{3+}$  ion are colourless, whereas those containing the  $\text{Ti}^{3+}$  ion are coloured. Explain.
- [A] Compare covalent size of the following  
(a) Nb  Ta

|        |                      |    |
|--------|----------------------|----|
| (b) Cr | <input type="text"/> | Mn |
| (c) Cu | <input type="text"/> | Zn |
| (d) Cu | <input type="text"/> | Ni |
| (e) Zr | <input type="text"/> | Hf |
| (f) Ca | <input type="text"/> | Sc |
| (g) Cr | <input type="text"/> | Mo |

- [B] Calculate effective nuclear charge of 3d-series elements (Sc—Zn)

|            | Screening constant(s) | Effective nuclear charge $Z^* = Z - S$ |
|------------|-----------------------|----------------------------------------|
| (a) Sc(21) | .....                 | .....                                  |
| (b) Ti(22) | .....                 | .....                                  |
| (c) V(23)  | .....                 | .....                                  |
| (d) Cr(24) | .....                 | .....                                  |
| (e) Mn(25) | .....                 | .....                                  |
| (f) Fe(26) | .....                 | .....                                  |
| (g) Co(27) | .....                 | .....                                  |
| (h) Ni(28) | .....                 | .....                                  |
| (i) Cu(29) | .....                 | .....                                  |
| (j) Zn(30) | .....                 | .....                                  |

- (a)  $\text{CrO}_5$  forms addition compound with pyridine in ethereal layer. What is structure of the addition product?  
(b) In ammoniacal solution, dichromate in presence of  $\text{H}_2\text{O}_2$  forms  $(\text{NH}_3)_3\text{CrO}_4$  in which Cr is in +IV state. What is structure?  
(c)  $\text{CrO}_3$  is used as cleansing agent for glassware. How is it prepared?  
(d) Give structure of  $\text{Cr}_2\text{O}_7^{2-}$  ion.
- What happens when  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  is heated? What is the type of reaction?
- Gas (A) and gas (B) both turns  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$  green. Gas (A) also turns lead acetate paper black. When gas (A) is passed into gas (B) in aqueous solution, yellowish white turbidity appears. Identify gas (A) and (B) and explain reactions.

16. If  $\text{CO}_2(g)$  under pressure is passed into  $\text{Na}_2\text{CrO}_4(aq)$ , yellow colour solution changes to orange-red solution. What is it due to? What is the function of  $\text{CO}_2(g)$ ?
17. Arrange the following ions in order of increasing strength as a reducing agent, and account for the trend:  
 (a)  $\text{Cr}^{2+}$  (b)  $\text{Cr}^{3+}$   
 (c)  $\text{Cr}_2\text{O}_7^{2-}$
18. (a)  $\text{Zn}^{2+}$  salts appear acidic due to hydrolysis. Identify acid and base in the following:  

$$[\text{Zn}(\text{H}_2\text{O})_4]^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{Zn}(\text{H}_2\text{O})_3\text{OH}]^+ + \text{H}_3\text{O}^+$$
  
 (b) Which other metal ion (other than  $\text{Zn}^{2+}$ ) behaves like  $[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$  in giving an acidic solution?
19. What happens if  $\text{NaHCO}_3$  is added to aqueous  $\text{ZnSO}_4$  solution?
20. Calculate magnetic moment of Mn in  $\text{MnO}_4^-$   
 ..... unpaired electrons on Mn in  $\text{MnO}_4^-$   
 ..... BM
21. Determine number of moles of  $\text{MnO}_4^-$  which are required to oxidise one mole of ferrous oxalate. Write reactions.  
 .....  
 .....
22. Rust stains contain  $\text{Fe}^{3+}$  salts ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ). These stains from fabric can be removed by the addition of oxalic acid. Explain.
23.  $\text{FeCl}_3$  solution gives  $\text{CO}_2$  with  $\text{NaHCO}_3$  solution. Explain.
24. How might you separate the following pairs of ions by addition of a single reagent?  
 (a)  $\text{Fe}^{3+}$  and  $\text{Na}^+$  (b)  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$   
 (d)  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$
25. (A) is a blue coloured hydrated salt giving white ppt. (B) with  $\text{BaCl}_2$ . 2.495 g of (A) gave 2.33 g of white ppt. (B). (A) gives deep reddish-brown solution on reaction with KI but after addition of hypo, reddish-brown solution appears in the form of white ppt. (C). (A) also gives chocolate coloured ppt. (D) with  $\text{K}_4[\text{Fe}(\text{CN})_6]$ . Identify (A) to (D) and explain reactions.
26. When aqueous KCN is added to aqueous  $\text{CuSO}_4$  solution, a white precipitate soluble in an excess of KCN, is formed. No precipitate is formed when  $\text{H}_2\text{S}$  gas is passed through the solution this point. Explain.
27.  $\Delta G_f^\circ$  (standard free energy of formation) of ZnO and CO are  $-318.2 \text{ kJ mol}^{-1}$  and  $-137.3 \text{ kJ mol}^{-1}$ . Is reduction of ZnO by carbon possible.
28. Colourless salt (A) gives white ppt. (B) with  $\text{NaOH}$ ; ppt. (B) dissolves in excess of  $\text{NaOH}$  to form (C). On passing  $\text{H}_2\text{S}$  gas into (C) white ppt. (D) appears.

(A) also gives white ppt (E) with  $\text{AgNO}_3$  solution. Identify (A) to (E).

29. Colourless salt (A)  $\xrightarrow{\Delta}$  (B) + (C) gas. (B) dissolves both in acid and alkali solution. Gas (C) turns lime water milky and acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution green. Ammoniacal solution of (A) gives white ppt. (D) with  $\text{H}_2\text{S}$  gas. Identify (A), (B), (C) and (D).
30. What is the advantage of using ZnO in paints instead of  $\text{Pb}^{2+}$  salts?
31. Compare thermal stability of ZnO, CdO and HgO.
32. Match the compounds in column (A) with their uses in column (B):

| Column A              | Column B                            |
|-----------------------|-------------------------------------|
| (I) ZnO               | (a) Metallurgical extraction of Ag. |
| (II) ZnO              | (b) Zerox printing.                 |
| (III) $\text{ZnSO}_4$ | (c) Luminous paints.                |
| (IV) Zn               | (d) Lithophone, eye lotion.         |

33. An impure metal is allowed to react with carbon monoxide at  $50^\circ\text{C}$  and the volatile gas thus formed is collected and heated further to about  $200^\circ\text{C}$ . This procedure gives the metal of 99.99% purity. What is the metal?

## Analytical Questions

- (a) Calculate number of moles of  $\text{MnO}_4^-$  required in acidic medium to oxidise :  
 (i) 1 mol of ferrous oxalate,  
 (ii) 1 mol of ferric oxalate.  
 (b) Calculate number of moles of  $\text{Cr}_2\text{O}_7^{2-}$  required in acidic medium to oxidise :  
 (i) 1 mol of ferrous oxalate,  
 (ii) 1 mol of ferric oxalate.

2. Black coloured solid (A)  $\xrightarrow[\Delta]{\text{KNO}_3 + \text{KOH}}$  green coloured solution (B)  
 $\downarrow \text{CO}_2$   
 (C) pink + (A)

(C) is decolorised by  $\text{Fe}^{2+}$ . Identify (A), (B) and (C) and explain reaction.

3. Mineral (A) + dil.  $\text{H}_2\text{SO}_4 \longrightarrow \text{soluble (B) or (C)} + (D), (\text{gas})$   
 $\text{soluble (B) or (C)} + \text{BaCl}_2 \text{ solution} \longrightarrow \text{white ppt. (E)}$   
 $\text{soluble (B) or (C)} + \text{K}_3[\text{Fe}(\text{CN})_6] \longrightarrow \text{blue ppt (F)}$   
 $\text{soluble (C)} + \text{aq NH}_3 \longrightarrow \text{deep blue solution (G)}$   
 $\text{(excess)}$   
 $\text{soluble (C)} + (D) \text{ gas} \longrightarrow \text{black ppt. (H) soluble in dil. HNO}_3$

What are (A) to (H) and explain reactions?

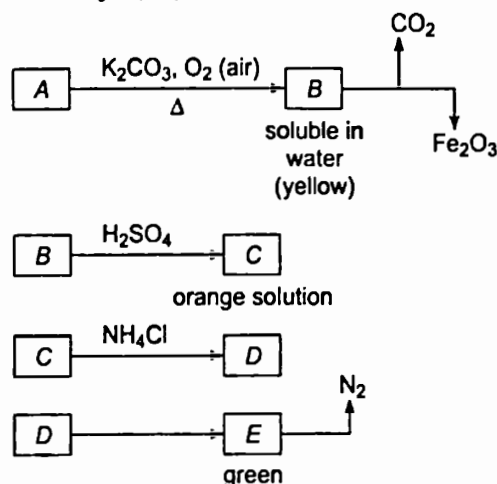
4. A student prepared three coordination compounds containing chromium with the following properties:

| Formula                                   | Colour      | Cl <sup>-</sup> ions in solution per formula unit |
|-------------------------------------------|-------------|---------------------------------------------------|
| (a) CrCl <sub>3</sub> · 6H <sub>2</sub> O | Violet      | 3                                                 |
| (b) CrCl <sub>3</sub> · 6H <sub>2</sub> O | Light green | 2                                                 |
| (c) CrCl <sub>3</sub> · 6H <sub>2</sub> O | Dark green  | 1                                                 |

Write modern formulae for these compounds and suggest a method for confirming the number of Cl<sup>-</sup> ions present in solution in each case.

5. Titanium, used in making jet aircraft engines, is much harder than potassium or calcium. Explain.
6. The highest oxidation state for the early transition metals Sc, Ti, V, Cr and Mn is the periodic group number. The highest oxidation state for the later transition elements Fe, Co, and Ni is less than the periodic group number. Explain.
7. (a) Which is stronger oxidising agent, Cr<sup>2+</sup> or Cu<sup>2+</sup>?  
 (b) Which is stronger reducing agent, V<sup>2+</sup> or Co<sup>2+</sup>?  
 (c) Which is more easily oxidised, Cr<sup>2+</sup> or Ni<sup>2+</sup>?  
 (d) Which is more easily reduced, Ti<sup>3+</sup> or Co<sup>3+</sup>?
8. Arrange the following substances in order of increasing strength as an oxidising agent, and account for the trend:  
 (a) Mn<sup>2+</sup> (b) MnO<sub>2</sub>  
 (c) MnO<sub>4</sub><sup>-</sup>
9. What product is formed when dilute H<sub>2</sub>SO<sub>4</sub>, a non oxidising acid is added to each of the following ions or compounds?  
 (a) CrO<sub>4</sub><sup>2-</sup> (b) Cr(OH)<sub>3</sub>  
 (c) Cr(OH)<sub>2</sub> (d) Fe(OH)<sub>2</sub>  
 (e) Cu(OH)<sub>2</sub>
10. Write a balanced net ionic equation for each of the following reactions:  
 (a) A CrO<sub>4</sub><sup>2-</sup> solution turns from yellow to orange upon addition of acid.  
 (b) Fe<sup>3+</sup>(aq) reacts with aqueous KSCN to give a deep red solution.  
 (c) Copper metal reacts with HNO<sub>3</sub> to give NO gas and a blue solution.  
 (d) A deep green solution of Cr(OH)<sub>3</sub> in excess base turns yellow on addition of H<sub>2</sub>O<sub>2</sub>.  
 (e) Dissolution of CuS in hot HNO<sub>3</sub> give NO gas, a blue solution and a yellow solid.
11. For each of the following reactions in acidic solution, predict the products and write a balanced net ionic equation:  
 (a) Co<sup>3+</sup>(aq) + H<sub>2</sub>O(l) →  
 (b) Cr<sup>2+</sup>(aq) + O<sub>2</sub>(g) →  
 (c) Cu(s) + Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>(aq) →

12. Identify A, B, C, D and E in the following :



## NCERT Problems

- Write down the electronic configuration of  
 (a) Cr<sup>3+</sup> (b) Cu<sup>+</sup>  
 (c) Co<sup>2+</sup> (d) Mn<sup>2+</sup>  
 (e) Pm<sup>3+</sup> (f) Ce<sup>4+</sup>  
 (g) Lu<sup>2+</sup> (h) Th<sup>4+</sup>
- Why are Mn<sup>2+</sup> compounds more stable than Fe<sup>3+</sup> towards oxidation to their +3 state?
- Explain briefly how +2 state becomes more and more stable in the first half of the first row transition element with increasing atomic number?
- To what extent do the electronic configuration decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with example.
- What may be the stable oxidation state of the transition element with the following *d*-electron configurations in the ground state of their atoms : 3d<sup>3</sup>, 3d<sup>5</sup>, 3d<sup>8</sup>, and 3d<sup>4</sup>?
- Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.
- What is lanthanoid contraction? What are the consequences of lanthanoid contraction?
- What are the characteristics of the transition elements and why are they called transition elements? Which of the *d*-block elements may not be regarded as the transition elements?
- In what way is the electronic configuration of the transition elements different from that of the non-transition elements?
- What are the different oxidation states exhibited by the lanthanoids?
- Explain giving reason  
 (a) Transition metals and many of their compounds show paramagnetic behaviour.



- (b) The enthalpies of atomisation of the transition metals are high.
- (c) The transition metals generally form coloured compounds.
- (d) Transition metals and their many compounds act as good catalyst.
12. What are interstitial compounds? Why are such compounds well known for transition metals?
13. How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples.
14. Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?
15. Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with
- (a) iodide (b) iron(II) solution
- (c)  $\text{H}_2\text{S}$
16. Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (a) iron(II) (b)  $\text{SO}_2$  (c) oxalic acid? Write the ionic equations for the reactions.
17. For  $M^{2+}/M$  and  $M^{3+}/M^{2+}$  systems that  $E^\ominus$  values for some metals are as follows :
- |                            |        |                                 |        |
|----------------------------|--------|---------------------------------|--------|
| $\text{Cr}^{2+}/\text{Cr}$ | -0.9 V | $\text{Cr}^{3+}/\text{Cr}^{2+}$ | -0.4 V |
| $\text{Mn}^{2+}/\text{Mn}$ | -1.2 V | $\text{Mn}^{3+}/\text{Mn}^{2+}$ | +1.5 V |
| $\text{Fe}^{2+}/\text{Fe}$ | -0.4 V | $\text{Fe}^{3+}/\text{Fe}^{2+}$ | +0.8 V |
- Use this data to comment upon :
- (a) The stability of  $\text{Fe}^{3+}$  in acid solution as compared to that of  $\text{Cr}^{3+}$  or  $\text{Mn}^{3+}$
- (b) The ease with which iron can be oxidised as compared to the similar process for either chromium or manganese metal.
18. Predict which of the following will be coloured in aqueous solution?  
 $\text{Ti}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{Cu}^+$ ,  $\text{Sc}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$  and  $\text{MnO}_4^-$ .  
 Give reason for each.
19. Compare the stability of +2 oxidation state for the elements of the first transition series.
20. Describe the chemistry of the three stages of photography, i.e., exposure, developing, and fixing.
21. Compare the chemistry of actinoids with that of the lanthanoids with special reference to
- (a) electronic configuration
- (b) oxidation state
- (c) atomic and ionic sizes and
- (d) chemical reactivity
22. How would you account for the following
- (a) Of the  $d^4$  species,  $\text{Cr}^{3+}$  is strongly reducing while manganese(III) is strongly oxidising.
- (b) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.
- (c) The  $d^1$  configuration is very unstable in ions.
23. What is meant by 'disproportionation'? Give two examples of disproportionation reaction in aqueous solution.
24. Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?
25. Calculate the number of unpaired electrons in following gaseous ions :  $\text{Mn}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{V}^{3+}$ , and  $\text{Ti}^{3+}$ . Which one of these is the most stable in aqueous solution?
26. Give example and suggest reason for the following features of the transition metal chemistry :
- (a) The lowest oxide of transition metal is basic, the highest is acidic.
- (b) A transition metal exhibits higher oxidation states in oxides and fluorides.
- (c) The highest oxidation state is exhibited in oxoanions of a metal.
27. Indicate the steps in the preparation of
- (a)  $\text{K}_2\text{Cr}_2\text{O}_7$  from chromite ore
- (b)  $\text{KMnO}_4$  from pyrolusite ore
- (c) Copper sulphate from metallic copper
- (d) Calomel from corrosive sublimate
28. What happens when aqueous ammonia reacts with
- (a) silver chloride
- (b) mercury (I) chloride
- (c) mercury (II) chloride?
29. Describe the two uses of each of the following
- (a) Copper sulphate (b) Silver nitrate
- (c) Silver bromide
30. What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.
31. What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements : 29, 59, 74, 95, 102, 104.
32. The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.
33. Which is the last element in the series of the actinoids? Write the electronic configuration of these elements. Comment on the possible oxidation state of this element.
34. Use Hund's rule to derive the electronic configuration of  $\text{Ce}^{3+}$  ion, and calculate the magnetic moment on the basis of 'spin-only' formula.
35. Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit

+2 oxidation states. Try to correlate this type of behaviour with the electronic configuration of these elements.

36. Compare the chemistry of the actinoids with that of lanthanoids with reference to :

- electronic configuration
- oxidation states, and
- chemical reactivity.

37. What is lanthanoid contraction? What is its effect on the chemistry of the elements which follow the lanthanoids?

38. Write the electronic configurations of the elements with the atomic number 61, 91, 101, and 109.

## Exercise 2

### (Stage 2 : High Skill Problem Solving)

#### Only One Option Correct

1. When KCN is added to  $\text{CuSO}_4$  solution

- KCN acts a reducing agent
- KCN acts as complexing agent
- $\text{K}_3[\text{Cu}(\text{CN})_4]$  is formed
- all of the above are correct

2. Out of  $\text{AgNO}_3$ ,  $\text{AgF}$  and  $\text{AgClO}_4$ , water soluble salts are

- $\text{AgF}$
- $\text{AgF}$ ,  $\text{AgNO}_3$
- $\text{AgF}$ ,  $\text{AgNO}_3$ ,  $\text{AgClO}_4$
- None of the above

3. Stability of  $\text{Cu}^+$  and  $\text{Ag}^+$  halide complexes are in order

- $\text{I} > \text{Br} > \text{Cl} > \text{F}$
- $\text{F} > \text{Cl} > \text{Br} > \text{I}$
- $\text{Cl} > \text{F} > \text{I} > \text{Br}$
- $\text{Br} > \text{I} > \text{Cl} > \text{F}$

4. Which of the following exists as white salt in anhydrous state?

- $\text{CuF}_2$
- $\text{CuSO}_4$
- Both (a) and (b)
- None of these

5. Which oxides will not give metal on heating?

- $\text{HgO}$
- $\text{ZnO}$
- $\text{Ag}_2\text{O}$
- All of these

6. When KI (excess) is added to

- I :  $\text{CuSO}_4$                       II :  $\text{HgCl}_2$   
 III :  $\text{Pb}(\text{NO}_3)_2$
- a white ppt. of  $\text{CuI}$  in I, a orange ppt.  $\text{HgI}_2$  in II and a yellow ppt.  $\text{PbI}_2$  in III
  - a white ppt. of  $\text{CuI}$  in I, an orange ppt. dissolving to  $\text{HgI}_4^{2-}$  in II, and a yellow ppt. of  $\text{PbI}_2$  in III
  - a white ppt. of  $\text{CuI}$ ,  $\text{HgI}_2$  and  $\text{PbI}_2$  in each case
  - None of the above is correct

7. Most common oxidation state of lanthanides is

- +2
- +3
- +4
- +5

8. The purest form of Fe is

- stainless steel
- steel
- cast iron
- wrought iron

9. In  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ , sodium nitroprusside,

- oxidation state of Fe is +2
- this has  $\text{NO}^+$  as ligand
- both (a) and (b) correct
- none of the above is correct

10.  $\text{FeSO}_4$  solution gives brown colour ring in testing nitrates or nitrites. This is

- $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$
- $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}_2]^{2+}$
- $[\text{Fe}(\text{H}_2\text{O})_4(\text{NO})_2]^{2+}$
- $[\text{Fe}(\text{H}_2\text{O})_4\text{NO}]^{2+}$

11.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  is actually

- $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_3$
- $[\text{Fe}(\text{H}_2\text{O}_5\text{Cl})\text{Cl}_2 \cdot \text{H}_2\text{O}$
- $[\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$
- $[\text{Fe}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$

12.  $\text{Ni}^{2+}$ , in traces, can be tested using

- sodium nitroprusside
- dimethyl glyoxime
- ammonium sulphocyanide
- potassium ferrocyanide

13.  $\text{CuSO}_4$  can be estimated volumetrically

- by reaction with KI followed by reaction with  $\text{Na}_2\text{S}_2\text{O}_3$
- by reaction with  $\text{BaCl}_2$
- by reaction with  $\text{K}_4\text{Fe}(\text{CN})_6$
- none of the above is correct

14. Which is correct statement?

- Ammoniacal  $\text{CuCl}$  is used to measure the amount of CO in gas samples
- Ammoniacal  $\text{CuCl}$  gives red ppt. with  $\text{CH}\equiv\text{CH}$
- Both (a) and (b) are correct
- None of the above is correct

15. Which is not true statement about  $\text{FeO}$ ?

- It is non-stoichiometric and is metal deficient
- It is basic oxide
- Its aqueous solution changes to  $\text{Fe}(\text{OH})_3$  and then to  $\text{Fe}_2\text{O}_3 \cdot (\text{H}_2\text{O})_n$  by atmospheric oxygen
- It gives red colour with KCNS

16. Match List I with List II and select the correct answer using the codes given below the lists:

**List I**  
(Metals)

- A. Zinc  
B. Tin  
C. Copper  
D. Magnesium

**List II**  
(Ores)

1. Azurite  
2. Carnallite  
3. Calamine  
4. Cassiterite

**Codes**

|     | A | B | C | D |
|-----|---|---|---|---|
| (a) | 3 | 4 | 2 | 1 |
| (b) | 3 | 4 | 1 | 2 |
| (c) | 4 | 1 | 3 | 2 |
| (d) | 4 | 3 | 2 | 1 |

17. Haemoglobin and chlorophyll contain respectively

- (a) Fe, Co (b) Fe, Mn  
(c) Mg, Fe (d) Fe, Mg

18. Due to lanthanide contraction

- (a) Fe, Co, Ni have equal size  
(b) Zr and Hf have equal size  
(c) all *f*-block ions have equal size  
(d) all isoelectronic ions have equal size

19. In  $\text{Cr}_2\text{O}_7^{2-}$  every Cr is linked to

- (a) two O atoms (b) three O atoms  
(c) four O atoms (d) five O atoms

20. For Ni and Pt different IP in  $\text{MJ mol}^{-1}$  are given below

|    | $(\text{IP})_1 + (\text{IP})_2$ | $(\text{IP})_3 + (\text{IP})_4$ |
|----|---------------------------------|---------------------------------|
| Ni | 2.49                            | 8.80                            |
| Pt | 2.60                            | 6.70                            |

hence:

- (a) nickel (II) compounds tend to be thermodynamically more stable than platinum (II)  
(b) platinum (IV) compounds tend to be more stable than nickel (IV)  
(c) both (a) and (b) are correct  
(d) none of the above is correct

21. Paramagnetism is given by the relation  $\mu = 2\sqrt{s(s+1)}$

magnetons where 's' is the total spin. On this basis, the paramagnetism of  $\text{Cu}^+$  ion is

- (a) 3.88 magnetons (b) 2.83 magnetons  
(c) 1.41 magnetons (d) zero

22. The oxygen carrying pigment, oxy-haemocyanin, containing two copper ions is diamagnetic, because

- (a) the two copper ions are in +1 oxidation state  
(b) one of the copper ions is in +1 oxidation state and the other is in +2 oxidation state  
(c) there are strong anti-ferromagnetic interactions between the two copper ions  
(d) there are ferromagnetic interactions between the two copper ions

23. Match List I with List II and select the correct answer using the codes given below the lists:

**List I**  
(Alloys)

- A. Gun metal  
B. German silver  
C. Brass  
D. Solder

**List II**

(Constituents)

1. Lead + tin  
2. Copper + tin + zinc  
3. Copper + zinc  
4. Copper + zinc + nickel

**Codes**

|     | A | B | C | D |
|-----|---|---|---|---|
| (a) | 1 | 3 | 4 | 2 |
| (b) | 4 | 2 | 1 | 3 |
| (c) | 2 | 4 | 3 | 1 |
| (d) | 3 | 1 | 2 | 4 |

24. An acidic solution contains  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$ . If hydrogen sulphide gas is passed through this solution, the precipitate will contain

- (a) CuS and ZnS (b) PbS and ZnS  
(c) CuS and PbS (d) CuS, PbS and ZnS

25.  $\text{Ti}^{2+}$  is purple while  $\text{Ti}^{4+}$  is colourless, because

- (a) there is no crystal field effect in  $\text{Ti}^{4+}$   
(b)  $\text{Ti}^{2+}$  has  $3d^2$  configuration  
(c)  $\text{Ti}^{4+}$  has  $3d^2$  configuration  
(d)  $\text{Ti}^{4+}$  is a very small cation when compared to  $\text{Ti}^{2+}$  and hence, does not absorb any radiation

26. Silver ornaments turn black by atmospheric

- (a)  $\text{O}_2$  (b)  $\text{N}_2$   
(c)  $\text{Cl}_2$  (d)  $\text{H}_2\text{S}$

27.  $\text{Cr}_2\text{O}_7^{2-} \xrightarrow{\text{pH}=x} \text{CrO}_4^{2-} \xrightarrow{\text{pH}=y} \text{Cr}_2\text{O}_7^{2-}$   
pH values *x* and *y* can be

- (a) 4 and 5 (b) 4 and 8  
(c) 8 and 4 (d) 8 and 9

28. In dilute alkaline solution  $\text{MnO}_4^-$  changes to

- (a)  $\text{MnO}_4^{2-}$  (b)  $\text{MnO}_2$   
(c)  $\text{Mn}_2\text{O}_3$  (d)  $\text{MnO}$

29.  $\text{Cl}_2$  gas is obtained by various reactions but not by

- (a)  $\text{KMnO}_4 + \text{conc. HCl} \xrightarrow{\Delta}$   
(b)  $\text{KCl} + \text{K}_2\text{Cr}_2\text{O}_7 + \text{conc. H}_2\text{SO}_4 \xrightarrow{\Delta}$   
(c)  $\text{MnO}_2 + \text{conc. HCl} \xrightarrow{\Delta}$   
(d)  $\text{KCl} + \text{F}_2 \longrightarrow$

30. Which is not true statement about  $\text{KMnO}_4$ ?

- (a) Its solution is unstable in acidic medium  
(b) Its small quantity added to conc.  $\text{H}_2\text{SO}_4$ , a green coloured solution containing  $\text{MnO}_3^+$  ions is formed  
(c)  $\text{MnO}_4^-$  changes to  $\text{Mn}^{2+}$  in basic solution  
(d) It is self-indicator in  $\text{Fe}^{2+}$  or  $\text{C}_2\text{O}_4^{2-}$  titration

31. Pyrolusite in  $\text{MnO}_2$  is used to prepare  $\text{KMnO}_4$ . Steps are :



I and II are

- (a) fuse with KOH/air, electrolytic oxidation
- (b) fuse with KOH/air, electrolytic reduction
- (c) fuse with conc HNO<sub>3</sub>/air, electrolytic reduction
- (d) all the above are correct

32. Fe is made passive by

- (a) dil. H<sub>2</sub>SO<sub>4</sub>
- (b) dil. HCl
- (c) aqua-regia
- (d) conc. H<sub>2</sub>SO<sub>4</sub>

33. Maximum magnetic moment is shown by

- (a) d<sup>6</sup>
- (b) d<sup>6</sup>
- (c) d<sup>7</sup>
- (d) d<sup>8</sup>

34. Magnetic moment of Cr (Z = 24), Mn<sup>+</sup> (Z = 25) and Fe<sup>2+</sup> (Z = 26) are x, y, z. They are in order

- (a) x < y < z
- (b) x = y < z
- (c) z < x = y
- (d) x = y = z

35. Interstitial compound is formed by

- (a) Fe, Co
- (b) Co, Ni
- (c) Fe, Ni
- (d) all of these

36. A jeweller is selling 22-carat gold articles with 95% purity, it is approximately

- (a) exact
- (b) 3.5% higher
- (c) 3.5% lower
- (d) 5% lower

37. Which is not true statement?

- (a) Ions of d-block elements are coloured due to d—d transition
- (b) Ions of f-block elements are coloured due to f—f transition
- (c) [Sc(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>, [Ti(H<sub>2</sub>O)<sub>6</sub>]<sup>4+</sup> are coloured complexes
- (d) Cu<sup>+</sup> is colourless ion

38. Match the catalysts in column X with their uses in column Y.

| Column X             | Column Y                                                                              |
|----------------------|---------------------------------------------------------------------------------------|
| A. TiCl <sub>4</sub> | 1. Adams catalyst in reduction                                                        |
| B. PdCl <sub>2</sub> | 2. in preparation of (CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>                |
| C. Pt/PtO            | 3. Reppe synthesis                                                                    |
| D. Cu                | 4. used as the ziegler-Natta catalyst in polythene production                         |
| E. Ni-complexes      | 5. Wacker process for converting C <sub>2</sub> H <sub>4</sub> to CH <sub>3</sub> CHO |

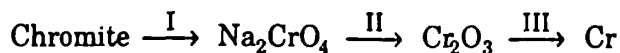
| A     | B | C | D | E |
|-------|---|---|---|---|
| (a) 4 | 5 | 1 | 2 | 3 |
| (b) 4 | 5 | 2 | 1 | 3 |
| (c) 5 | 4 | 1 | 3 | 2 |
| (d) 2 | 1 | 3 | 5 | 4 |

39. When (A) NH<sub>4</sub>VO<sub>3</sub> is heated.

(B) (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is heated

- (a) in both cases N<sub>2</sub> is formed
- (b) in both cases NH<sub>3</sub> is formed
- (c) in (A) NH<sub>3</sub> and in (B) N<sub>2</sub> are formed
- (d) in (A) N<sub>2</sub> and in (B) NH<sub>3</sub> are formed

40. FeCr<sub>2</sub>O<sub>4</sub> (chromite) is converted to Cr by following steps:



I, II and III are

- | I                                            | II                    | III   |
|----------------------------------------------|-----------------------|-------|
| (a) Na <sub>2</sub> CO <sub>3</sub> /air, Δ  | C                     | C     |
| (b) NaOH/air, Δ                              | C, Δ                  | Al, Δ |
| (c) NaOH/air, Δ                              | C, Δ                  | Mg, Δ |
| (d) conc. H <sub>2</sub> SO <sub>4</sub> , Δ | NH <sub>4</sub> Cl, Δ | C, Δ  |

41. When H<sub>2</sub>O<sub>2</sub> is added to an acidified solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

- (a) solution turns green due to formation of Cr<sub>2</sub>O<sub>3</sub>
- (b) solution turns yellow due to formation of K<sub>2</sub>CrO<sub>4</sub>
- (c) a deep blue-violet coloured compound CrO(O<sub>2</sub>)<sub>2</sub> is formed
- (d) solution gives green ppt. of Cr(OH)<sub>3</sub>

42. Out of SiCl<sub>4</sub>, TiCl<sub>4</sub>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup>, CCl<sub>4</sub> isostructural are

- (a) SiCl<sub>4</sub>, TiCl<sub>4</sub>
- (b) SO<sub>4</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup>
- (c) both (a) and (b)
- (d) None of these

43. Maximum oxidation state is shown by

- (a) Os
- (b) Mn
- (c) Cr
- (d) Co

44. Following elements do not show the properties characteristic of d-block elements

- (a) Cu, Ag, Au
- (b) Zn, Hg, Cd
- (c) Sc, Ti, V
- (d) Fe, Co, Ni

45. The ability of d-block elements to form complexes is due to

- (a) small and highly charged ions
- (b) vacant low energy orbitals to accept lone pair of electrons from ligands
- (c) both (a) and (b) are correct
- (d) None of the above is correct

46. AgCl and NaCl are colourless. NaBr and NaI are also colourless but AgBr and AgI are coloured. This is due to

- (a) Ag<sup>+</sup> polarises Br<sup>-</sup> and I<sup>-</sup>
- (b) Ag<sup>+</sup> has unpaired d-orbital
- (c) Ag<sup>+</sup> depolarises Br<sup>-</sup> and I<sup>-</sup>
- (d) None of above is correct

47. Which is correct statement?

- (a) In less acidic solution K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and H<sub>2</sub>O<sub>2</sub> give violet coloured diamagnetic [CrO(O<sub>2</sub>)(OH)]<sup>-</sup> ion
- (b) In alkaline H<sub>2</sub>O<sub>2</sub>, K<sub>3</sub>CrO<sub>8</sub> (with tetraperoxo species) [Cr(O<sub>2</sub>)<sub>4</sub>]<sup>3-</sup> is formed
- (c) In ammoniacal solution, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> gives (NH<sub>3</sub>)<sub>3</sub>CrO<sub>4</sub>
- (d) All of the above are correct statements

48. Match the compounds of column X with oxidation state of column Y.

| Column X |                                                |   |   | Column Y |
|----------|------------------------------------------------|---|---|----------|
| A.       | $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ |   |   | 5        |
| B.       | $\text{CrO}_5$                                 |   |   | 4        |
| C.       | $\text{K}_3\text{CrO}_8$                       |   |   | 6        |
| D.       | $(\text{NH}_3)_3\text{CrO}_4$                  |   |   | 3        |
|          | A                                              | B | C | D        |
| (a)      | 3                                              | 6 | 5 | 4        |
| (b)      | 3                                              | 4 | 5 | 6        |
| (c)      | 4                                              | 5 | 6 | 3        |
| (d)      | 6                                              | 5 | 4 | 3        |

49. For  $\text{CrO}_3$  following is not true statement

- (a) it is called chromic acid  
 (b) it is colourless due to  $3d^{10}$  configuration  
 (c) it is bright orange solid and colour arises due to charge transfer  
 (d) it is toxic and corrosive

50. Only +2, +3, +4 oxidation states are shown by

- (a) Sc, Ti (b) Fe, Ni  
 (c) Ti, Ni (d) Zn, Ni

51. Coagulation of blood takes place by

- (a) ferric alum (b) potash alum  
 (c) both (a) and (b) (d) None of these

52. When KCN comes in contact with blood, one dies immediately, it is due to

- (a)  $\text{CN}^-$  forms stable complex with iron of haemoglobin of blood  
 (b)  $\text{CN}^-$  combines with  $\text{H}_2\text{O}$  of blood causing it poison  
 (c) both (a) and (b) are correct  
 (d) None of the above is correct

53.  $\text{MnO}_4^-$  is of intense pink colour, though Mn is in (+7) oxidation state. It is due to

- (a) oxygen gives colour to it  
 (b) charge transfer when Mn gives its electron to oxygen  
 (c) charge transfer when oxygen gives its electron to Mn making it Mn (+VI) hence, coloured  
 (d) None of the above is correct

54. Out of  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Ni}(\text{CO})_4]$

- (a) all have identical geometry  
 (b) all are paramagnetic  
 (c) all are diamagnetic  
 (d)  $[\text{Fe}(\text{CN})_6]^{4-}$  is diamagnetic but  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Ni}(\text{CO})_4]$  are paramagnetic

55. In  $[\text{Fe}(\text{CN})_5(\text{NO}^+)]^{2-}$ , Fe has +3 state. It can be decided by

- (a) magnetic measurement  
 (b) colligative property  
 (c) colour  
 (d) hybridisation

56. In 3d transition series, if nuclear charge increases, the screening effect

- (a) increases  
 (b) decreases  
 (c) first decreases and then increases  
 (d) first increases and then decreases

57. Maximum oxidation state of Os is

- (a) +6 (b) +7  
 (c) +8 (d) +5

58. Which forms interstitial compound?

- (a) Fe (b) Co  
 (c) Ni (d) All of these

59. Which shows maximum magnetic moment among the bivalent ions of the first transition series?

- (a)  $\text{Fe}^{2+}$  (b)  $\text{Co}^{2+}$   
 (c)  $\text{Ni}^{2+}$  (d)  $\text{Mn}^{2+}$

60. Select incorrect statement(s).

- (a) Ionisation energies of 5d-elements are greater than those of 3d and 4d elements  
 (b) Cu(I) is diamagnetic while Cu(II) is paramagnetic  
 (c)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is coloured while  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  is colourless  
 (d) Transition elements cannot form complexes

61. Guignet's green is

- (a)  $\text{NiO} \cdot 2\text{H}_2\text{O}$  (b)  $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$   
 (c)  $\text{CuSO}_4 \cdot 2\text{H}_2\text{O}$  (d)  $\text{CrO} \cdot 2\text{H}_2\text{O}$

62. Which of the following metals has more than one oxidation state?

- (a) Zn (b) Mn  
 (c) Sr (d) Ca

63. Which of the following metals have only one oxidation state?

- (a) Co (b) Fe  
 (c) Sc (d) Al

64. Which of the following compounds is amphoteric?

- (a)  $\text{Cr}(\text{OH})_2$  (b)  $\text{Fe}(\text{OH})_2$   
 (c)  $\text{Cr}(\text{OH})_3$  (d)  $\text{Fe}(\text{OH})_3$

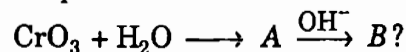
65. Increasing basic properties of  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{HfO}_2$  are in order

- (a)  $\text{TiO}_2 < \text{ZrO}_2 < \text{HfO}_2$  (b)  $\text{HfO}_2 < \text{ZrO}_2 < \text{TiO}_2$   
 (c)  $\text{HfO}_2 < \text{TiO}_2 < \text{ZrO}_2$  (d)  $\text{ZrO}_2 < \text{TiO}_2 < \text{HfO}_2$

66. Which is called chromic acid?

- (a) CrO (b)  $\text{Cr}_2\text{O}_3$   
 (c)  $\text{CrO}_3$  (d)  $\text{CrO}_2$

67. What are the species A and B in the following



- (a)  $\text{H}_2\text{CrO}_4$ ,  $\text{H}_2\text{Cr}_2\text{O}_7$  (b)  $\text{H}_2\text{Cr}_2\text{O}_7$ ,  $\text{Cr}_2\text{O}_3$   
 (c)  $\text{CrO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$  (d)  $\text{H}_2\text{Cr}_2\text{O}_7$ ,  $\text{CrO}_4^{2-}$

68. Very recently (in Aug 2003), IUPAC has approved the name of the element of atomic number 110. Name of the element is

- (a) Darmstadtium (b) Mountanium  
 (c) Rhenium (d) Bhorium

69. The element Ds lies in  
 (a) s-block (b) p-block  
 (c) d-block (d) f-block
70. The element Ds lies below... in the Periodic Table  
 (a) W (b) Hg  
 (c) Pt (d) Au
71. Which one of the following statements is not correct?  
 (a) Zinc dissolves in sodium hydroxide solution  
 (b) Carbon monoxide reduces iron (III) oxide to iron  
 (c) Mercury (II) iodide dissolves in excess of potassium iodide solution  
 (d) Tin(IV) chloride is made by dissolving tin solution in concentrated hydrochloric acid
72. Which of the following statements concerning lanthanides elements is false?  
 (a) Lanthanides are separated from one another by ion-exchange method  
 (b) Ionic radii of trivalent lanthanides steadily increase with increase in the atomic number  
 (c) All lanthanides are highly dense metals  
 (d) More characteristic oxidation state of lanthanides elements is +3
73. The mercury is the only metal which is liquid at 0°C. This is due to its  
 (a) weak metallic bond (b) high ionization energy  
 (c) high vapour pressure (d) both (a) and (b)
74. A transition element X has a configuration  $[\text{Ar}]3d^4$ , in its +3 oxidation state. Its atomic number is  
 (a) 25 (b) 26  
 (c) 22 (d) 19
75. Which of the following elements is responsible for oxidation of water to  $\text{O}_2$  is biological processes?  
 (a) Fe (b) Cu  
 (c) Mn (d) Mo
76. Which one of the following ionic species will impart colour to an aqueous solution?  
 (a)  $\text{Ti}^{4+}$  (b)  $\text{Cu}^+$   
 (c)  $\text{Zn}^{2+}$  (d)  $\text{Cr}^{3+}$
77. Which of the following statements is not correct?  
 (a)  $\text{La}(\text{OH})_3$  is less basic than  $\text{Lu}(\text{OH})_3$   
 (b) In lanthanide series ionic radius of  $\text{Ln}^{3+}$  ion decreases  
 (c) La is actually an element of transition series rather lanthanide  
 (d) Atomic radius of Zr and Hf are same because of lanthanide contraction
78. The correct order of ionic radii of  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Lu}^{3+}$  is  
 (Atomic number of Y = 39, La = 57, Eu = 63, Lu = 71)  
 (a)  $\text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+} < \text{Y}^{3+}$   
 (b)  $\text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+} < \text{Y}^{3+}$   
 (c)  $\text{Y}^{3+} < \text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+}$   
 (d)  $\text{Y}^{3+} < \text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+}$
79. Which one of the following characteristics of the transition metals is associated with their catalytic activity?  
 (a) Colour of hydrated ions  
 (b) Variable oxidation states  
 (c) High enthalpy of atomization  
 (d) Paramagnetic behaviour
80. The basic character of the transition metal monoxides follows the order  
 (Atomic number Ti = 22, V = 23, Cr = 24, Fe = 26)  
 (a)  $\text{TiO} > \text{FeO} > \text{VO} > \text{CrO}$   
 (b)  $\text{TiO} > \text{VO} > \text{CrO} > \text{FeO}$   
 (c)  $\text{TiO} > \text{CrO} > \text{TiO} > \text{FeO}$   
 (d)  $\text{CrO} > \text{VO} > \text{FeO} > \text{TiO}$
81. Voids are  
 (a) 14 elements in the sixth period (atomic no. = 90 to 103) that are filling 4f-sublevel  
 (b) 14 elements in the seventh period (atomic no. = 90 to 103) that are filling 5f-sublevel  
 (c) 14 elements in the sixth period (atomic no. = 58 to 71) that are filling 4f-sublevel  
 (d) 14 elements in the seventh period (atomic no. = 58 to 71) that are filling 4f-sublevel
82. Among K, Ca, Fe and Zn, the element which can form more than one binary compound with chlorine is  
 (a) Fe (b) Zn  
 (c) K (d) Ca
83. Philosopher's wool on treatment with cobalt nitrate, produces  
 (a)  $\text{CoBaO}_2$  (b)  $\text{CoZnO}_2$   
 (c)  $\text{CoSrO}_2$  (d)  $\text{CoMgO}_2$
84. Which of the following does not react with  $\text{AgCl}$ ?  
 (a)  $\text{NH}_4\text{OH}$  (b)  $\text{NaNO}_3$   
 (c)  $\text{Na}_2\text{S}_2\text{O}_3$  (d)  $\text{Na}_2\text{CO}_3$
85. Which of the following is used as purgative?  
 (a)  $\text{HgS}$  (b)  $\text{Hg}_2\text{Cl}_2$   
 (c)  $\text{HgCl}_2$  (d)  $\text{ZnSO}_4$
86. The reactivity of transition elements decreases with  
 (a) the decrease in the atomic number  
 (b) the increase in the atomic number  
 (c) low heat of hydration  
 (d) None of the above
87. Fulminating gold is  
 (a)  $\text{AuCl}_3$  (b)  $\text{Au}_2\text{S}$   
 (c)  $\text{Au}(\text{NH}_2)=\text{NH}$  (d)  $\text{H}[\text{Au}(\text{Cl})_4]$
88. An extremely hot copper wire reacts with steam to produce  
 (a)  $\text{Cu}_2\text{O}$  (b)  $\text{CuO}_2$   
 (c)  $\text{Cu}_2\text{O}_2$  (d)  $\text{CuO}$
89. Ag is obtained from  $\text{AgNO}_3$  with  
 (a)  $\text{NH}_3$  (b)  $\text{PH}_3$   
 (c)  $\text{AsH}_3$  (d)  $\text{Na}_2\text{CO}_3$

90. The incorrect statement for *d*-block element is  
 (a) it shows magnetic property  
 (b) it has variable valency  
 (c) it has tendency of formation of coloured ions  
 (d) it has complete *d*-orbitals
91. Which of the following transition element shows the highest oxidation state?  
 (a) Mn (b) Fe  
 (c) V (d) Cr
92. To protect iron against corrosion, the most durable metal plating on it, is  
 (a) nickel plating (b) tin plating  
 (c) copper plating (d) zinc plating
93.  $K_2Cr_2O_7$  on heating with aqueous NaOH, gives  
 (a)  $CrO_4^{2-}$  (b)  $Cr(OH)_3$   
 (c)  $Cr_2O_7^{2-}$  (d)  $Cr(OH)_2$
94. The lanthanide contraction is responsible for the fact that  
 (a) Zn and Y have about the same radii  
 (b) Zr and Nb have similar oxidation state  
 (c) Zr and Hf have about the same radii  
 (d) Zr and Zn have the same oxidation state
95. The electronic configuration of (Gd) (At. no. 64) is  
 (a)  $[Xe] 4f^8, 5d^9, 6s^2$  (b)  $[Xe] 4f^7, 5d^1, 6s^2$   
 (c)  $[Xe] 4f^6, 5d^2, 6s^2$  (d)  $[Xe] 4f^3, 5d^3, 6s^2$
96. Which one of the following elements shows maximum number of different oxidation states in its compounds?  
 (a) Eu (b) La  
 (c) Gd (d) Am
97. Oxidation state of Fe in  $Fe_3O_4$  is  
 (a)  $\frac{3}{2}$  (b)  $\frac{4}{5}$   
 (c)  $\frac{5}{4}$  (d)  $\frac{8}{3}$
98. Bell-metal is an alloy of  
 (a) Cu + Pb (b) Cu + Sn  
 (c) Cu + Zn (d) Cu + Ni
99. Of the following transition metals, the maximum number of oxidation states are exhibited by  
 (a) chromium ( $Z = 24$ ) (b) manganese ( $Z = 25$ )  
 (c) iron ( $Z = 26$ ) (d) titanium ( $Z = 22$ )
100. Philosopher's wool on heating with BaO at  $1100^\circ C$  produce  
 (a) Ba +  $ZnCl_2$  (b) BaCdO<sub>2</sub>  
 (c) BaZnO<sub>2</sub> (d) BaO<sub>2</sub> + Zn
101. The nature of  $Fe_2O_3$  is  
 (a) acidic (b) basic  
 (c) amphoteric (d) None of these
102. The metal present in vitamin B<sub>12</sub> is  
 (a) cobalt (b) iron  
 (c) manganese (d) magnesium
103. Which among the following is consumed by humans in the elemental form?  
 (a) Cu (b) Pb  
 (c) Ag (d) Hg
104. Anhydrous ferric chloride is prepared by  
 (a) heating hydrated ferric chloride at a high temperature in a stream of air  
 (b) heating metallic iron in a stream of dry chlorine gas  
 (c) reaction of ferric oxide with HCl  
 (d) reaction of metallic iron with HCl
105. When  $MnO_2$  is fused with KOH and  $KNO_3$ , a coloured compound is formed, the product and its colour is  
 (a)  $K_2MnO_4$ , green (b)  $KMnO_4$ , purple  
 (c)  $Mn_2O_3$ , brown (d)  $Mn_3O_4$ , black
106.  $(NH_4)_2Cr_2O_7$  on heating gives a gas which is also given by  
 (a) heating  $NH_4NO_2$  (b) heating  $NH_4NO_3$   
 (c)  $Mg_3N_2 + H_2O$  (d)  $Na + H_2O_2$
107. The pair of compounds having metals in their highest oxidation state is  
 (a)  $MnO_2, FeCl_3$   
 (b)  $[MnO_4]^- , CrO_2Cl_2$   
 (c)  $[Fe(CN)_6]^{3-}, [Co(CN)_3]$   
 (d)  $[NiCl_4]^{2-}, [CoCl_4]^-$
108. The compound having tetrahedral geometry is  
 (a)  $[Ni(CN)_4]^{2-}$  (b)  $[Pd(CN)_4]^{2-}$   
 (c)  $[PdCl_4]^{2-}$  (d)  $[NiCl_4]^{2-}$
109. Spin only magnetic moment of the compound  $Hg[Co(SCN)_4]$  is  
 (a)  $\sqrt{3}$  (b)  $\sqrt{15}$   
 (c)  $\sqrt{24}$  (d)  $\sqrt{8}$
110. Which pair of compounds is expected to show similar colour in aqueous medium?  
 (a)  $FeCl_3$  and  $CuCl_2$  (b)  $VOCl_2$  and  $CuCl_2$   
 (c)  $VOCl_2$  and  $FeCl_2$  (d)  $FeCl_2$  and  $MnCl_2$
111. A solution of a metal ion when treated with KI gives a red precipitate which dissolves in excess KI to give a colourless solution. Moreover, the solution of metal ion on treatment with a solution of cobalt(II) thiocyanate gives rise to a deep blue crystalline precipitate. The metal ion is  
 (a)  $Pb^{2+}$  (b)  $Hg^{2+}$   
 (c)  $Cu^{2+}$  (d)  $Co^{2+}$
112. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is  
 (a) 3 (b) 4  
 (c) 5 (d) 6

113. Consider following statements,  
 I. The size of the lanthanide  $M^{3+}$  ions decreases as the atomic number of  $M$  increases.  
 II. Electronic spectra of lanthanides show very broad bands.  
 III. As with transition metals, coordination number six is very common in lanthanide complexes.  
 Which of the statements given above is/are correct?  
 (a) I only (b) I and II  
 (c) I and III (d) III only
114. A red solid is insoluble in water. However, it becomes soluble if some KI is added to water. Heating the red solid in a test tube results in liberation of some violet coloured fumes and droplets of a metal appear on the cooler parts of the test tube. The red solid.  
 (a)  $(NH_4)_2Cr_2O_7$  (b)  $HgI_2$   
 (c)  $HgO$  (d)  $Pb_3O_4$
115. What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid?  
 (a)  $Cr^{3+}$  and  $Cr_2O_7^{2-}$  are formed  
 (b)  $Cr_2O_7^{2-}$  and  $H_2O$  are formed  
 (c)  $CrO_4^{2-}$  is reduced to +3 state of Cr  
 (d) None of the above
116. Which one of the following nitrates will leave behind a metal on strong heating?  
 (a) Ferric nitrate (b) Copper nitrate  
 (c) Manganese nitrate (d) Silver nitrate
117. Cerium ( $Z = 58$ ) is an important member of lanthanides. Which of the following statements about cerium is incorrect?  
 (a) The common oxidation states of cerium are +3 and +4  
 (b) The +3 oxidation states of cerium is more stable than the +4 state  
 (c) The +4 oxidation state of cerium is not known in solutions  
 (d) Cerium (IV) acts as an oxidising agent
118. Calomel ( $Hg_2Cl_2$ ) on reaction with ammonium hydroxide gives  
 (a)  $HgO$  (b)  $Hg_2O$   
 (c)  $NH_2-Hg-Hg-Cl$  (d)  $HgNH_2Cl$
119. Which of the following factors may be regarded as the main cause of lanthanide contraction?  
 (a) Greater shielding of 5d-electron by 4f-electrons  
 (b) Poorer shielding of 5d-electron by 4f-electrons  
 (c) Effective shielding of one 4f-electrons by another in the subshell  
 (d) Poor shielding of one of 4f-electrons by another in the subshell
120. Amongst the following, identify the species with an atom in +6 oxidation state  
 (a)  $MnO_4^-$  (b)  $Cr(CN)_6^{3-}$   
 (c)  $NiF_6^{2-}$  (d)  $CrO_2Cl_2$
121. When  $MnO_2$  is fused with  $KOH$  and  $KClO_3$ , a coloured compound is formed, the product and its colour is  
 (a)  $K_2MnO_4$ , green (b)  $KMnO_4$ , purple  
 (c)  $Mn_2O_3$ , brown (d)  $Mn_3O_4$  black
122.  $CrO_2Cl_2$  is formed while testing  
 (a)  $NO_3^-$  (b)  $Cl^-$   
 (c)  $Cr^{3+}$  (d)  $Fe^{3+}$
123. The most abundant element is  
 (a) Cu (b) Hg  
 (c) Cd (d) Fe
124. Which represents correct comparison of the stability of ions?  
 (a)  $MnO_4^- < Mn^{2+}$  (b)  $Cr^{2+} < Cr^{3+}$   
 (c)  $CrO_4^{2-} < Cr^{3+}$  (d) All of these
125. On August 2003, IUPAC approved the name of the element with atomic number 110 as  
 (a) Ds (b) Mt  
 (c) Uun (d) Nnu
126. Different (variable) oxidation state is shown by transition elements. It is due to the fact  
 (a)  $(n-1)d$  electrons may be excited to  $ns$  orbital  
 (b)  $ns$  electrons may be excited to  $(n-1)d$  orbitals  
 (c)  $(n-1)d$ -electron may get involved along with  $ns$  electrons in bonding  
 (d) none of the above facts is correct
127. Select correct statement for the lesser number of oxidation states in 3d-series.  
 (a) In the beginning of the series it can be due to the presence of too few electrons to lose or share  
 (b) Towards the end of the series, it can be ascribed to the presence of too many electrons and thus fewer empty orbitals to share electrons with the ligands  
 (c) Both (a) and (b) are correct  
 (d) None of the above is correct
128. In which case(s) there is change in oxidation number  
 (a) Aqueous solution of  $CrO_4^{2-}$  is acidified  
 (b)  $SO_2$  gas is passed into  $Cr_2O_7^{2-}/H^+$   
 (c)  $Cr_2O_7^{2-}$  solution is made alkaline  
 (d)  $CrO_2Cl_2$  is dissolved in  $NaOH$
129. Factors which affect the stability of the compounds are  
 (a) the energy of sublimation  
 (b) the lattice energy  
 (c) the solvation energy  
 (d) all of the above
130. Which forms protective and non-corrosive oxide layer?  
 (a) Cr (b) Ni  
 (c) Zn (d) Cu



- 131.** First *IE* of 5*d*-elements are higher than those of 3*d* and 4*d*-elements. This is due to  
 (a) greater effective nuclear charge acting on outer valence electrons  
 (b) greater effective nuclear charge is experienced because of the weak shielding of the nucleus by 4*f*-electrons  
 (c) both (a) and (b)  
 (d) None of the above
- 132.**  $\text{NH}_4\text{Cl}$  is used to clear metal surfaces because  
 (a) it dissociates into  $\text{NH}_3$  and  $\text{HCl}$  on heating  
 (b)  $\text{NH}_3$  forms soluble complexes with the metal  
 (c)  $\text{HCl}$  forms a volatile  
 (d) None of the above
- 133.** Most transition metals  
 I : forms sets of compounds which display different oxidation states of the metal.  
 II : form coloured ions in solution  
 III : burn vigorously in oxygen  
 IV : replace  $\text{H}_2$  from dilute acids  
 of these  
 (a) I, II, III are correct  
 (b) II, III, IV and correct  
 (c) I, II are correct  
 (d) all are correct
- 134.** A blue solution of copper sulphate becomes darker when treated with excess of ammonia. This is because  
 (a) ammonia molecules replace water molecules in the solution  
 (b) ammonia is stronger ligand than water  
 (c) ammonia forms a stable complex ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  with  $\text{Cu}^{2+}$  ions.  
 (d) all of the above are correct
- 135.** Effective atomic number (EAN) of Fe in brown ring complex  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$   
 (a) 36 (b) 37  
 (c) 38 (d) 39
- 136.** Select the correct relative stability.  
 (a)  $[\text{Cu}(\text{CN})_4]^{3-} > [\text{Cd}(\text{CN})_4]^{3-}$   
 (b)  $\text{PtCl}_4^{2-} > \text{NiCl}_4^{2-}$   
 (c)  $[\text{NiCl}_6]^{2-} > [\text{PtCl}_6]^{2-}$   
 (d)  $[\text{Cd}(\text{CN})_4]^{2-} > [\text{Cu}(\text{CN})_4]^{3-}$
- 137.** Magnetic moment of  $[\text{Ni}(\text{CN})_4]^{2-}$  is zero but that of  $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$  is 2.83 BM.  
 It is because of  
 (a) different oxidation state of Ni in two complexes  
 (b)  $\text{CN}^-$  is a strong ligand making two unpaired electrons in  $\text{Ni}^{2+}$  paired while in  $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$ , two electrons remain unpaired  $\text{H}_2\text{O}$  being weak ligand  
 (c) both (a) and (b)  
 (d) none of the above
- 138.** There are three electrons unpaired in  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  and calculated value of magnetic moment is 3.87 BM, which is quite different from the experimental value of 4.40 BM. This is because of  
 (a) increase in number of unpaired electrons  
 (b) some contribution of the orbital motion of the electron to the magnetic moment  
 (c) change in orbital spin of the electron  
 (d) *d-d*\* transition
- 139.**  $\text{Cu}^{2+}$  has a stronger polarising power than that of  $\text{Ca}^{2+}$  because  
 (a)  $\text{Cu}^{2+}$  ion is smaller than  $\text{Ca}^{2+}$  ion  
 (b)  $\text{Ca}^{2+}$  has inert gas configuration whereas  $\text{Cu}^{2+}$  ion does not  
 (c) copper shows variable valency, calcium does not  
 (d)  $\text{Cu}^{2+}$  is smaller than  $\text{Ca}^{2+}$  ion and the *d*-electrons in  $\text{Cu}^{2+}$  ion shield the nucleus poorly
- 140.** Atoms of the transition elements are smaller than those of the *s*-block elements. This is because of  
 (a) usual contraction in size across a horizontal period  
 (b) orbital electrons added to the penultimate *d*-shell rather than to the outer shell of the atom  
 (c) both (a) and (b)  
 (d) none of the above
- 141.** Select correct order of sizes of different species.  
 (a)  $\text{Zr} = \text{Hf}$ ;  $\text{Nb} = \text{Ta}$ ;  $\text{Fe} = \text{Co} = \text{Ni}$   
 (b)  $\text{Zr}^{4+} < \text{Zr}$ ;  $\text{Nb}^{3+} < \text{Ta}^{3+}$ ;  $\text{Fe}^{3+} < \text{Fe}^{2+} < \text{Fe}$   
 (c)  $\text{Zr}^{4+} = \text{Hf}^{4+}$ ;  $\text{Nb}^{3+} = \text{Ta}^{3+}$ ;  $\text{Fe} < \text{Co} < \text{Ni}$   
 (d)  $\text{Zr}^{4+} < \text{Hf}^{4+}$   $\text{Nb}^{3+} = \text{Ta}^{3+}$ ,  $\text{Ni} < \text{Cu} < \text{Co}$
- 142.** The radii of the elements from chromium ( $Z = 24$ ) to copper ( $Z = 29$ ) are very close to one another. This is due to  
 (a) lanthanide contraction  
 (b) the fact that successive addition of *d*-electrons screen the outer electrons (4*s*) from the inward pull of the nucleus  
 (c) increase in radii due to increase in *n* is compensated by decrease in radii due to increase in *Z*  
 (d) atomic radii do not remain constant but decrease in a normal gradation
- 143.** The lanthanoid contraction is due to  
 (a) filling of 4*f* before 4*d*  
 (b) filling of 4*d* before 4*f*  
 (c) filling of 4*f* before 5*d*  
 (d) filling of 5*d* before 4*f*
- 144.** Magnetic moment of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is  
 (a) 1.73 BM (b) 2.83 BM  
 (c) 3.87 BM (d) 4.90 BM
- 145.** Magnetic moment of Fe is similar to that of  
 (a)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  (b)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$   
 (c) both (a) and (b) (d) None of these

146. The atomic numbers of vanadium (V), chromium (Cr), manganese (Mn) and iron are respectively 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionization enthalpy?

- (a) V (b) Cr  
(c) Mn (d) Fe

147. There are three unpaired electrons in  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and calculated value of magnetic moment is 3.87 BM which is quite different from the experimental value of 4.40 BM. This is because of

- (a) increase in number of unpaired electrons  
(b) some contribution of the orbital motion of the electron to the magnetic moment  
(c) change in orbital spin of the electron  
(d)  $d-d^*$  transition

148. Increasing value of magnetic moments of (I)  $\text{Ni}(\text{CO})_4$ , II :  $[\text{Ti}(\text{H}_2\text{O})_6]^{2+}$ , III :  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ , IV :  $[\text{V}(\text{H}_2\text{O})_6]^{2+}$  is

- (a)  $\text{I} < \text{II} < \text{III} < \text{IV}$  (b)  $\text{IV} < \text{III} < \text{II} < \text{I}$   
(c)  $\text{II} < \text{III} < \text{I} < \text{IV}$  (d)  $\text{II} < \text{I} < \text{III} < \text{IV}$

149. Which of the following is colourless?

- (a)  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  (b)  $[\text{V}(\text{H}_2\text{O})_6]^{2+}$   
(c)  $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$  (d)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

150. Which is the coloured ion?

- (a)  $[\text{Cu}(\text{CN})_4]^{3-}$  (b)  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$   
(c)  $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$  (d) All of these

151. Oxidation state of Mn in  $\text{MnO}_4^-$  is +7 indicating all electrons paired in Mn but  $\text{MnO}_4^-$  is coloured. It is due to

- (a) charge transfer  
(b) presence of unpaired electron in  $d$ -orbital in oxygen  
(c) both (a) and (b)  
(d) none of the above

152. Which of the following is paramagnetic as well as coloured ion?

- (a)  $\text{Cu}^+$  (b)  $\text{Cu}^{2+}$   
(c)  $\text{Sc}^{3+}$  (d)  $\text{Ti}^{4+}$

153. Select correct statement(s).

- (a) Coloured the ion arises due to  $d-d^*$  transition  
(b) Colour we observe is the complimentary colour absorbed by the compound  
(c) Both (a) and (b) are correct  
(d) None of the above is correct

154. Nonstoichiometry is shown

- (a) due to variable valency of transition elements  
(b) due to defects in solid structures  
(c) due to both (a) and (b)  
(d) due to none of the above

155. Cementite is

- (a) interstitial compound of iron and carbon  
(b) an alloy of Fe and Cr  
(c) a compound resembling cement  
(d) an ore of iron

156. Which catalyst is matched according to its name and function?

| Catalyst                                 | Name             | Function                            |
|------------------------------------------|------------------|-------------------------------------|
| (a) $\text{TiCl}_4$                      | Fenton's reagent | Oxidation of alcohols               |
| (b) $\text{FeSO}_4/\text{H}_2\text{O}_2$ | Ziegler-Natta    | Polythene preparation               |
| (c) Pd/C                                 | Lindlar          | Hydrogen to give <i>cis</i> -alkene |
| (d) Pt/PtO                               | Adam             | Synthesis of $\text{CH}_3\text{OH}$ |

157. Select correct statement.

- (a) Fe and Mo atoms are present in nitrogen fixing enzymes  
(b) A cobalt atom lies at the centre of the vitamin  $\text{B}_{12}$  coenzyme  
(c) Fe atoms are involved in the ferredoxins of photosynthetic process  
(d) All of the above are correct statements

158. Which is the set of nonstoichiometric compounds?

- (a) NaCl, FeO,  $\text{MgCl}_2$   
(b) FeO, CuS, VSe  
(c)  $\text{Fe}_3\text{O}_4$ , NaCl, CuS  
(d) CuCl, CuS, MgO

159. Which one of the following elements is the main metallic constituent of haemoglobin?

- (a) Al (b) Cu  
(c) Fe (d) Mn

160.  $\text{KMnO}_4$  is the oxo salt of

- (a)  $\text{MnO}_2$  (b)  $\text{Mn}_2\text{O}_7$   
(c)  $\text{MnO}_3$  (d)  $\text{Mn}_2\text{O}_3$

161.  $\text{CrO}_3$  liberates  $\text{CO}_2$  with  $\text{Na}_2\text{CO}_3$  solution. Thus,  $\text{CrO}_3$  is

- (a) an acidic oxide  
(b) a basic oxide  
(c) an amphoteric oxide  
(d) a nonstoichiometric oxide

162.  $\text{VO}_2$  is an amphoteric oxide and in acidic medium it forms

- (a)  $\text{VO}^{2+}$  (b)  $\text{VO}_2^+$   
(c)  $\text{V}^{3+}$  (d)  $\text{VO}_2^{2+}$

163.  $\text{CrO}_2^{2+}$  is the cation from

- (a) CrO (b)  $\text{Cr}_2\text{O}_3$   
(c)  $\text{CrO}_5$  (d)  $\text{CrO}_3$

164. The oxide  $\text{Cr}_2\text{O}_3$  is

- (a) acidic (b) amphoteric  
(c) basic (d) ozonide

165. At pH = 4,  $\text{Cr}_2\text{O}_4^{2-}$  exists as

- (a)  $\text{CrO}_4^{2-}$  (b)  $\text{CrO}_3$   
(c)  $\text{CrO}_2^{2+}$  (d)  $\text{Cr}_2\text{O}_7^{2-}$

166. At pH = 12,  $\text{Cr}_2\text{O}_7^{2-}$  changes to

- (a)  $\text{CrO}_3$  (b)  $\text{CrO}_2^{2+}$   
(c)  $\text{CrO}_4^{2-}$  (d) no change

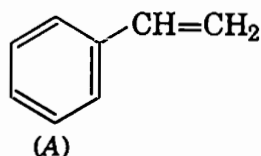
167. In acidic medium  $\text{H}_2\text{O}_2$  changes  $\text{K}_2\text{Cr}_2\text{O}_7$  to  $\text{CrO}_5$  (deep violet solution in ether) having two peroxy linkage. Oxidation number of Cr in  $\text{CrO}_5$  is  
 (a) +10 (b) -10  
 (c) +4 (d) +6

168. In alkaline  $\text{H}_2\text{O}_2$ ,  $\text{Cr}_2\text{O}_7^{2-}$  changes to tetraperoxo species ... having oxidation number of Cr as ...  
 (a)  $\text{CrO}_4^{2-}$  6  
 (b)  $\text{CrO}_5$  6  
 (c)  $\text{CrO}_8^{3-}$  5  
 (d)  $\text{CrO}_8^{3-}$  11

169.  $\text{MnO}_4^{2-}$  can be converted to  $\text{MnO}_4^-$   
 (a) by oxidation with  $\text{Cl}_2$   
 (b) by electrochemical oxidation at anode  
 (c) by both (a) and (b) methods  
 (d) by none of the above methods

170. In acidic medium  $\text{MnO}_4^{2-}$   
 (a) disproportionates to  $\text{MnO}_2$  and  $\text{MnO}_4^-$   
 (b) is oxidised to  $\text{MnO}_4^-$   
 (c) is reduced to  $\text{MnO}_2$   
 (d) is reduced to  $\text{Mn}^{2+}$

171. Alkaline  $\text{KMnO}_4$  (Baeyer's reagent) can be used to test unsaturation in (A).



In this case

- (a) unsaturation in side-chain is affected  
 (b) unsaturation in benzene nucleus is affected  
 (c) unsaturation in both is affected  
 (d) Baeyer's reagent cannot be used
172.  $\text{KMnO}_4$  spot can be bleached by  
 (a)  $\text{H}_2\text{O}_2/\text{H}^+$  (b)  $\text{SO}_2/\text{H}^+$   
 (c)  $\text{C}_2\text{O}_4^{2-}/\text{H}^+$  (d) all of these
173. Traces of  $\text{MnO}_4^-$  in conc.  $\text{H}_2\text{SO}_4$  may change to  
 (a)  $\text{Mn}_2\text{O}_7$  (b)  $\text{MnO}_3^+$   
 (c)  $\text{MnO}_2$  (d)  $\text{MnO}_4^{2-}$
174. A white solid Y, on heating gives off a gas which turns lime water milky; the residue is yellow when hot; white when cold. The solid Y is probably  
 (a)  $\text{ZnCO}_3$  (b)  $\text{PbCO}_3$   
 (c)  $\text{ZnSO}_4$  (d)  $\text{Zn(NO}_3)_2$
175. Aqueous  $\text{ZnO}$  can neutralise  $\text{HCl}$  as well as  $\text{NaOH}$  solution. Thus,  $\text{ZnO}$  is an  
 (a) acidic oxide (b) basic oxide  
 (c) amphoteric oxide (d) amphiprotic oxide
176. Which is not blackened by atmosphere  $\text{H}_2\text{S}$ ?  
 (a)  $\text{Pb(CH}_3\text{COO)}_2$  (b)  $\text{Zn(CH}_3\text{COO)}_2$   
 (c)  $\text{Cu(CH}_3\text{COO)}_2$  (d)  $\text{Hg(CH}_3\text{COO)}_2$

177.  $\text{ZnO}$  in  $\text{CH}_3\text{COOH}$  gives bluish white ppt. with X. X is  
 (a)  $\text{K}_4[\text{Fe(CN)}_6]$  (b)  $\text{K}_3[\text{Fe(CN)}_6]$   
 (c)  $\text{Na}_2[\text{Fe(CN)}_5\text{NO}]$  (d)  $\text{Fe(CO)}_5$

178. Select correct statement.  
 (a)  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  is called Epsom salt  
 (b)  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  is isomorphous with Glauber's salt  
 (c)  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  with  $\text{BaS}$  is called lithophone  
 (d) All the above are correct statements

179. Silver nitrate solution is kept in brown bottles in the laboratory because  
 (a) it reacts with ordinary bottles  
 (b) ordinary bottles catalyse the decomposition  
 (c) the materials of brown bottles do not react with it  
 (d) brown bottles cut the passage of light through it

180. On addition of  $\text{AgNO}_3$  to four different test tubes containing different solutions, one of them gave a white precipitate. It may be  
 (a)  $\text{CHCl}_3$  (b)  $\text{CaCl}_2$   
 (c)  $\text{KNO}_3$  (d)  $\text{CCl}_4$

181. Select correct statement.  
 (a)  $\text{PH}_3$  reduces  $\text{AgNO}_3$  to metallic Ag  
 (b) Organic tissues turn  $\text{AgNO}_3$  black by reducing it to Ag  
 (c)  $\text{AgCN}$  is soluble in  $\text{KCN}$   
 (d) All of the above are correct statements

182. Hypo ( $\text{Na}_2\text{S}_2\text{O}_3$ )  
 (a) dissolves  $\text{AgBr}$  in photographic plate  
 (b) gives white precipitate with  $\text{AgNO}_3$ ; white precipitate changes to black on dilution  
 (c) gives both reactions  
 (d) gives none of the above reactions

183. Sugar in urine sample can be detected by  
 I : Fehling's solution  
 II : Benedict's solution  
 III : Tollen's solution.  
 Select correct alternate  
 (a) I, II, III (b) I, III  
 (c) I, II (d) II, III

184. If a person is asked to prepare the blue print of a building plan, he can use  
 (a)  $\text{FeCl}_3 + \text{K}_4[\text{Fe(CN)}_6]$   
 (b)  $\text{FeCl}_2 + \text{K}_3[\text{Fe(CN)}_6]$   
 (c)  $\text{FeCl}_2 + \text{K}_4[\text{Fe(CN)}_6]$   
 (d)  $\text{Fe(Ct)} + \text{K}_3[\text{Fe(CN)}_6]$  Ct is citrate

185. If  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  would exist as a complex, one mole of it in aqueous solution on reaction with excess of  $\text{AgNO}_3$  forms  
 (a) 1 mole of  $\text{AgCl}$  (white precipitate)  
 (b) 2 moles of  $\text{AgCl}$   
 (c) 3 moles of  $\text{AgCl}$   
 (d) no reaction

186.  $K_3[Fe(CN)_6]$  is used as an external indicator in the dichromate estimation of  $Fe^{2+}$ . Following change is observed  
 (a) colourless to blue (b) blue to red  
 (c) colourless to red (d) blue to colourless
187. If zinc pieces are added yellow  $FeCl_3$  solution, it turns to very light green. It is because  
 (a)  $FeCl_3$  solution is acidic due to hydrolysis and zinc added produces nascent hydrogen causing reduction of  $FeCl_3$  to  $FeCl_2$   
 (b)  $FeCl_3$  solution is basic and zinc added produces  $H_2$  which reduces  $FeCl_3$  to  $FeCl_2$   
 (c) Zinc reduces  $FeCl_3$  to  $FeCl_2$   
 (d) none of the above is correct
188. At  $300^\circ C$ ,  $FeCl_3$   
 (a) decomposes into  $FeCl_2$  and  $Cl_2$   
 (b) decomposes into  $Fe$  and  $Cl_2$   
 (c) sublimes to give liquid  $FeCl_3$   
 (d) sublimes to give gaseous dimer  $(FeCl_3)_2$
189. The compound that get oxidised even on exposure to air is  
 (a)  $Fe_2O_3$  (b)  $FeCl_2$   
 (c)  $FeCl_3$  (d)  $Fe_2(SO_4)_3$
190. Rust contains  $Fe_2O_3 \cdot H_2O$ . Rust spots can be removed by  
 (a)  $Na_2S_2O_3$  (hypo) (b)  $SO_2$   
 (c)  $H_2C_2O_4$  (oxalic acid) (d)  $KMnO_4$
191. Select correct statement(s).  
 (a)  $\alpha\text{-}Fe_2O_3$  has hexagonally close-packed lattice of  $O^{2-}$  ions with  $Fe^{3+}$  ions in two-thirds of the octahedra holes.  
 (b)  $\gamma\text{-}Fe_2O_3$  has cubic close-packed arrangement of  $O^{2-}$  ion with  $Fe^{3+}$  ions randomly distributed in both the octahedral and tetrahedral sites.  
 (c)  $Fe_3O_4$ ,  $Fe_2O_3$  and  $FeO$  all and tend to be non-stoichiometric.  
 (d) All the above are correct statements
192. On passing  $Cl_2$  gas into alkaline hydrated  $Fe_2O_3$  solution  
 (a) red purple solution of  $Na_2FeO_4$  is formed  
 (b) colourless  $NaFeO_2$  is formed due to dissolution of  $Fe_2O_3$  into  $NaOH$   
 (c)  $Fe(OH)_3$  is formed  
 (d) no reaction takes place
193.  $Fe_3O_4$  is called  
 (a) haematite (b) magnetite  
 (c) cassiterite (d) dolomite
194. Isomorphous salts are  
 (a) green vitriol, blue vitriol and Epsom salt  
 (b) green, vitriol, white vitriol and blue vitriol  
 (c) green vitriol, white vitriol and Epsom salt  
 (d) blue vitriol, white vitriol and Epsom salt
195.  $[Fe(H_2O)_5NO]^{2+}$  is brown-ring complex in  $NO_3^-$ . In this complex  
 (a)  $NO$  transfers its electron to  $Fe^{2+}$  so that there are three electrons unpaired making iron as  $Fe(I)$  and nitrosyl as  $NO^+$   
 (b) magnetic moment of  $Fe$  is 3.87 BM  
 (c) the colour is due to charge transfer  
 (d) all of the above are correct statements
196.  $K_2Cr_2O_7/H^+$  changes to green by  
 (a)  $Fe^{2+}$  (b)  $SO_3^{2-}$   
 (c) both (a) and (b) (d) none of these
197. Some of the following reagents are used as **primary standard**.  
 I :  $KMnO_4$ ; II :  $NaOH$ ; III :  $K_2Cr_2O_7$ ;  
 IV :  $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ ; V :  $H_2C_2O_4 \cdot 2H_2O$   
 Select primary standard  
 (a) all except II, IV (b) all except I, II  
 (c) all except I, II, III (d) only IV
198. One mole of  $FeC_2O_4$  is oxidised by  $KMnO_4$  in acidic medium. Number of moles of  $KMnO_4$  used are  
 (a) 0.6 mol (b) 1.2 mol  
 (c) 0.4 mol (d) 1 mol
199. Fehling's solution consists of two separate alkaline solutions. One solution contains  $CuSO_4$ . The other solution contains.  
 (a)  $NaHCO_3$  (b)  $KNaC_4H_4O_6$   
 (c)  $KHCO_3$  (d)  $K_2CO_3$
200. If  $H_2S$  gas is passed into a solution of  $Cu^{2+}$ ,  $Cd^{2+}$  having excess of  $KCN$   
 (a)  $CuS$  and  $CdS$  both are precipitated  
 (b) soluble complex  $[Cu(CN)_4]^{3-}$  and  $[Cd(CN)_4]^{2-}$  are formed and no effect of passing  $H_2S$  gas  
 (c) soluble complex  $[Cu(CN)_4]^{3-}$  and  $[Cd(CN)_4]^{2-}$  as are formed, of which  $CdS$  is precipitated as yellow ppt.  
 (d) soluble complex  $[Cu(CN)_4]^{3-}$  and  $[Cd(CN)_4]^{2-}$  are formed of which  $CuS$  is precipitated as black ppt.
201. When  $K_2CrO_4$  is added to  $CuSO_4$  solution, there is formation of  $CuCrO_4$  as well as  $CuCr_2O_7$ . Formation of  $CuCr_2O_7$  is due to  
 (a) basic nature of  $CuSO_4$  solution which converts  $CrO_4^{2-}$  to  $Cr_2O_7^{2-}$   
 (b) acidic nature of  $CuSO_4$  solution which converts  $CrO_4^{2-}$  to  $Cr_2O_7^{2-}$   
 (c)  $CuSO_4$  has the typical property of converting  $CuCrO_4$  is formed to  $CuCr_2O_7$   
 (d) no  $CuCr_2O_7$  is formed
202. In an atmosphere with industrial smog,  $Cu$  corrodes to  
 (a) basic sulphate  $Cu_2(OH)_2SO_4$   
 (b) basic carbonate  $Cu_2(OH)_2CO_3$   
 (c) both (a) and (b)  
 (d) none of the above

**203.**  $\text{Na}_2\text{S}_2\text{O}_3$ 

- (a) reduces  $\text{Cu}^{2+}$  to  $\text{Cu}^+$   
 (b) reduces  $\text{I}_2$  to  $\text{I}^-$   
 (c) complexes  $\text{AgBr}$  as  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$   
 (d) undergoes all the above are correct

**204.** The element which forms ions in dimeric state is

- (a) iron (b) mercury  
 (c) cadmium (d) nickel

**205.** Mixture is supposed to contain nitrates of  $\text{Pb}^{2+}$  and  $\text{Hg}_2^{2+}$ . On adding dil.  $\text{HCl}$  both are precipitated as white precipitate

Select correct statement(s).

- (a)  $\text{PbCl}_2$  (white precipitate) is soluble in hot water and formation of yellow precipitate on adding  $\text{KI}$  to hot solution confirms  $\text{Pb}^{2+}$   
 (b)  $\text{Hg}_2\text{Cl}_2$  is blackened by  $\text{NH}_3$ , and changes to  $\text{HgCl}_2$  by aqua-regia.  $\text{HgCl}_2$  can be detected by  $\text{KI}$  when orange precipitate soluble in excess of  $\text{KI}$  is formed.  
 (c) both tests are conclusive  
 (d) none of the tests is conclusive

**206.**  $\text{Hg}_2\text{Cl}_2$  ionises as ..... and cation has ..... unpaired electron(s)

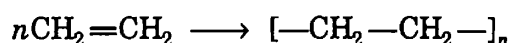
- (a)  $2\text{Hg}^+$  and  $2\text{Cl}^-$ , two (b)  $\text{Hg}_2^{2+}$  and  $2\text{Cl}^-$ , two  
 (c)  $\text{Hg}_2^{2+}$  and  $2\text{Cl}^-$ , one (d)  $\text{Hg}_2^{2+}$  and  $2\text{Cl}^-$ , no

**207.** Alkaline  $\text{NH}_4\text{Cl}$  solution reacts with  $\text{K}_2\text{HgI}_4$  (Nessler's reagent) forming

- (a)  $(\text{HgNH}_2\text{Cl} + \text{Hg})$  — black  
 (b)  $\left[ \text{O} \begin{array}{c} \text{Hg} \\ \diagup \quad \diagdown \\ \text{Hg} \end{array} \text{N} \begin{array}{c} \text{H} \\ \diagdown \quad \diagup \\ \text{H} \end{array} \right] \text{I}$  — brown iodide of Millon's base  
 (c)  $\text{K}_2[\text{O}—\text{Hg}—\text{NH}_2\text{Cl}] \text{I}$  — brown iodide of Millon's base  
 (d) none of the above

**208.**  $\text{HgCl}_2$  is soluble in

- (a) cold water  
 (b)  $\text{NaCl}$  solution due to formation of  $\text{HgCl}_4^{2-}$   
 (c) both (a) and (d)  
 (d) none of the above

**209.** In the following reaction

Catalyst is

- (a) Adam (b) Ziegler-Natta  
 (c)  $\text{Ni/Pd}$  (d)  $\text{Fe/Mo}$

**210.**  $\text{TiCl}_4$  is a

- (a) Bronsted-Lowry acid (b) Bronsted-Lowry base  
 (c) Lewis acid (d) Lewis base

**211.** Which of the following are sets of diamagnetic species?

- (a)  $\text{TiCl}_4$ ,  $\text{O}_2$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$

- (b)  $\text{TiCl}_4$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $\text{CO}$ ,  $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$   
 (c)  $\text{TiCl}_4$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $\text{CO}$   
 (d)  $\text{TiCl}_4$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $\text{O}_2$

**212.** Which are not blackened by atmospheric  $\text{H}_2\text{S}$ ?

- (a)  $\text{TiO}_2$  (b)  $\text{ZnO}$   
 (c)  $\text{ZnSO}_4 + \text{BaS}$  (d) All of these

**213.** Elements after atomic number 92 are called

- (a) lanthanoids  
 (b) actinoids  
 (c) inner-transition elements  
 (d) transuranium elements

**214.**  $\text{Ln}^{3+}$  (trivalent lanthanide ions) have EC

- (a)  $[\text{Xe}] 4f^1$  to  $[\text{Xe}] 4f^{14}$   
 (b)  $[\text{Xe}] 4d^1 4f^1$  to  $[\text{Xe}] 4d^1 4f^{14}$   
 (c)  $[\text{Xe}] 4d^2 4f^0$  to  $[\text{Xe}] 4d^1 4f^{14}$   
 (d)  $[\text{Xe}] 4f^0$  to  $[\text{Xe}] 4f^{14}$

**215.** A certain metal will liberate hydrogen from dilute acids. It will react with water to form hydrogen only when the metal is heated and the water is in the form of steam. The metal is probably

- (a) iron (b) potassium  
 (c) copper (d) mercury

**216.** The magnetic moment  $\mu$ , of transition metals is related to the number of unpaired electrons,  $n$  as

- (a)  $\mu = n(n+2)^2$  (b)  $\mu = n^2(n+2)$   
 (c)  $\mu = \frac{n}{(n+2)}$  (d)  $\mu = \sqrt{n(n+2)}$

**217.** Misch metal is

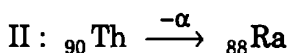
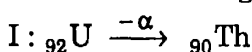
- (a) an alloy of lanthanide and copper  
 (b) an alloy of lanthanide and nickel  
 (c) an alloy of lanthanide, iron and carbon  
 (d) an alloy of calcium and copper

**218.** Which of the following have completely filled  $5f$  orbitals?

- (a)  $\text{No}$  (b)  $\text{Lr}$   
 (c) Both (a) and (b) (d) None of these

**219.**  $\text{An}^{3+}$  (trivalent actinoid ions) have configuration

- (a)  $5f^0$  to  $5f^{14}$  (b)  $5f^1$  to  $5f^{14}$   
 (c)  $5f^2$  to  $5f^{14}$  (d)  $5f^0$  to  $5f^{13}$

**220.** Consider following radioactive decay of

In which case group of the parent and daughter element remains unchanged?

- (a) in I (b) in II  
 (c) in both (a) and (b) (d) in none of these

**221.** Select correct statement(s).

- (a)  $\text{Pu}^{4+}$  disproportionates to  $\text{Pu}^{3+}$  and  $\text{PuO}_2^{2+}$  in strongly acidic solution  
 (b) Maximum oxidation state of  $\text{Np}$  is +7

- (c)  $\text{UO}_2^{2+}$  is stable  
(d) All of the above are correct statement
222. Uranium reacts with conc.  $\text{HNO}_3$   
(a) to give  $\text{U}(\text{NO}_3)_4$  and  $\text{H}_2$   
(b) to give  $\text{U}(\text{NO}_3)_2$  and  $\text{NO}_2$   
(c)  $\text{UO}_2(\text{NO}_3)_2$  and  $\text{H}_2$   
(d) to make metal passive
223. Which of the following statements is not correct?  
(a)  $\text{La}(\text{OH})_3$  is less basic than  $\text{Lu}(\text{OH})_3$   
(b) In lanthanide series ionic radius of  $\text{Ln}^{3+}$  ion decreases  
(c) La is actually an element of transition series rather lanthanide  
(d) Atomic radius of Zr and Hf are same because of lanthanide contraction
224. Lanthanoids are  
(a) 14 elements in the sixth period (atomic number = 90 to 103) that are filling 4f-sublevel  
(b) 14 elements in the seventh period (atomic no. = 90 to 103) that are filling 5f-sublevel  
(c) 14 elements in the sixth period (atomic no. = 58 to 71) that are filling 4f-sublevel  
(d) 14 elements in the seventh period (atomic no. = 58 to 71) that are filling 4f-sublevel
225. Four successive members of the first row transition elements are listed below with their atomic numbers. Which one of them is expected to have the highest third ionization enthalpy?  
(a) Vanadium ( $Z = 23$ )      (b) Chromium ( $Z = 24$ )  
(c) Iron ( $Z = 26$ )          (d) Manganese ( $Z = 25$ )
226. The number of moles of  $\text{KMnO}_4$  reduced by one mole of KI in alkaline medium is  
(a) one fifth                  (b) five  
(c) one                         (d) two
227. The main reason for larger number of oxidation state exhibited by the actinides than that corresponding lanthanides, is  
(a) lesser energy difference between 5f and 6d orbitals than between 4f and 5d-orbitals  
(b) larger atomic size of actinides than the lanthanides  
(c) more energy difference between 5f and 6d orbitals than between 4f and 5d-orbitals  
(d) greater reactive nature of the actinides than the lanthanides
228. The common oxidation state of the elements of lanthanide series is  
(a) +1                         (b) +3  
(c) +4                         (d) +6
229. The metal that does not displace hydrogen from an acid is  
(a) Al                         (b) Ca  
(c) Zn                         (d) Hg
230. Ferric sulphate is represented by which formula?  
(a)  $\text{FeSO}_4$                     (b)  $\text{FeSO}_3$   
(c)  $\text{Fe}(\text{SO}_4)_2$                 (d)  $\text{Fe}_2(\text{SO}_4)_3$
231. The transition metal with least atomic number  
(a) Os                         (b) Zr  
(c) Pt                         (d) Ru
232. Lanthanide and actinides resemble in  
(a) electronic configuration  
(b) oxidation state  
(c) ionisation energy  
(d) formation of complexes
233. Stainless steel is an alloy of  
(a) Cu                         (b) Ni and Cr  
(c) Mn                         (d) Zn
234. Solder is an alloy of  
(a) 70% lead 30% tin      (b) 30% lead, 70% tin  
(c) 80% lead, 20% tin      (d) 90% copper, 10% tin
235. Which of the following is a highly corrosive salt?  
(a)  $\text{FeCl}_2$                     (b)  $\text{PbCl}_2$   
(c)  $\text{Hg}_2\text{Cl}_2$                     (d)  $\text{HgCl}_2$
236. Which of the following is potassium ferricyanide?  
(a)  $\text{K}_4[\text{Fe}(\text{CN})_6]$           (b)  $\text{K}_3[\text{Fe}(\text{CN})_6]$   
(c)  $\text{K}_3[\text{Fe}(\text{CN})_3]$           (d)  $\text{K}_3[\text{Fe}(\text{CN})_4]$
237. German silver is an alloy of  
(a) Fe, Cr, Ni                (b) Ag, Cu, Au  
(c) Cu, Zn, Ni                (d) Cu, Zn, Sn
238. The Mohr's salt is shown by  
(a)  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$   
(b)  $\text{FeSO}_4(\text{NH}_3)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$   
(c)  $\text{K}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
(d)  $\text{FeSO}_2(\text{NH}_2)_4\text{SO}_4 \cdot 6\text{H}_2\text{O}$
239. The composition of duralumin is  
(a) Al 94%, Mg 6%  
(b) Cu 56%, Zn 24%, Ni 20%  
(c) Cu 95, Al 5%  
(d) Al 95%, Cu 4%, Mn 0.5%, Mg 0.5%
240. Lanthanide for which +II and +III oxidation states are common is  
(a) La                         (b) Nd  
(c) Ce                         (d) Eu
241. The colourless species is  
(a)  $\text{VCl}_3$                     (b)  $\text{VOSO}_4$   
(c)  $\text{Na}_3\text{VO}_4$                 (d)  $[\text{V}(\text{H}_2\text{O})_6]\text{SO}_4 \cdot \text{H}_2\text{O}$
242.  $\text{MnO}_4^{2-}$  (1 mol) in neutral aqueous medium disproportionates to  
(a)  $\frac{2}{3}$  mol of  $\text{MnO}_4^-$  and  $\frac{1}{3}$  mol of  $\text{MnO}_2$   
(b)  $\frac{1}{3}$  mol of  $\text{MnO}_4^-$  and  $\frac{2}{3}$  mol of  $\text{MnO}_2$

- (c)  $\frac{1}{3}$  mol of  $\text{Mn}_2\text{O}_7$  and  $\frac{1}{7}$  mol of  $\text{MnO}_2$   
 (d)  $\frac{2}{3}$  mol of  $\text{Mn}_2\text{O}_7$  and  $\frac{1}{3}$  mol of  $\text{MnO}_2$
243. An aqueous solution of  $\text{CoCl}_2$  on addition of excess of concentrated  $\text{HCl}$  turn blue due to formation of  
 (a)  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]$  (b)  $[\text{Co}(\text{H}_2\text{O})_2\text{Cl}_4]^{2-}$   
 (c)  $[\text{CoCl}_4]^{2-}$  (d)  $[\text{Co}(\text{H}_2\text{O})_2\text{Cl}_2]$
244. The diamagnetic species is  
 (a)  $[\text{Ni}(\text{CN})_4]^{2-}$  (b)  $[\text{NiCl}_4]^{2-}$   
 (c)  $[\text{CoCl}_4]^{2-}$  (d)  $[\text{CoF}_6]^{2-}$
245. Among the following pairs of ions, the lower oxidation state in aqueous solutions is more stable than the other in  
 (a)  $\text{Ti}^+$ ,  $\text{Ti}^{3+}$  (b)  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$   
 (c)  $\text{Cr}^{2+}$ ,  $\text{Cr}^{3+}$  (d)  $\text{V}^{2+}$ ,  $\text{VO}^{2+}$
246. The colour imparted by  $\text{Co(II)}$  compounds to glass is  
 (a) green (b) deep blue  
 (c) yellow (d) red
247. Given below, catalyst and corresponding process/reaction are matched. The mismatch is  
 (a)  $[\text{RhCl}(\text{PPh}_3)_2]$  : Hydrogenation  
 (b)  $\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$  : Polymerisation  
 (c)  $\text{V}_2\text{O}_5$  : Haber-Bosch process  
 (d) Nickel : Hydrogenation
248.  $\text{KI}$  and  $\text{CuSO}_4$  solutions on mixing produce  
 (a)  $\text{Cu}_2\text{I}_2 + \text{K}_2\text{SO}_4$  (b)  $\text{Cu}_2\text{I}_2 + \text{KI}_3 + \text{K}_2\text{SO}_4$   
 (c)  $\text{CuI}_2 + \text{K}_2\text{SO}_4$  (d)  $\text{CuI}_2 + \text{KI}_3 + \text{K}_2\text{SO}_4$
249. The reactivity of transition elements decreases with  
 (a) the decrease in the atomic number  
 (b) the increase in the atomic number  
 (c) low heat of hydration  
 (d) None of the above
250. Catalyst used in making  $\text{H}_2\text{SO}_4$  in contact process is  
 (a)  $\text{V}_2\text{O}_5$  (b)  $\text{Fe}_2\text{O}_3$   
 (c)  $\text{Cr}_2\text{O}_3$  (d)  $\text{CrO}_3$
251. The incorrect configuration is  
 (a)  $\text{K} = [\text{Ar}] 4s^1$  (b)  $\text{Cr} = [\text{Ar}] 3d^5, 4s^1$   
 (c)  $\text{Cr} = [\text{Ar}] 3d^4, 4s^2$  (d)  $\text{Cu} = [\text{Ar}] 3d^{10}, 4s^1$
252. By annealing, steel  
 (a) becomes soft  
 (b) becomes liquid  
 (c) becomes hard and brittle  
 (d) is covered with a thin film of  $\text{Fe}_3\text{O}_4$
253. Transition metals show paramagnetism due to  
 (a) characteristic configuration  
 (b) high lattice energy  
 (c) variable oxidation states  
 (d) unpaired electrons
254. The oxides,  $\text{CrO}_3$ ,  $\text{MoO}_3$  and  $\text{WO}_3$  are strongly  
 (a) neutral (b) acidic  
 (c) basic (d) None of these
255. The outer electronic configuration of transition elements is  
 (a)  $(n-1)s^2nd^{1-2}$   
 (b)  $(n+1)s^2nd^{1-5}$   
 (c)  $(n-1)s^2p^6(n-1)d^{1-10}, ns^{1,2}$   
 (d)  $ns^2(n+1)d^{1-10}$
256. The highest magnetic moment will be shown by  
 (a) Ni (b) Co  
 (c) Fe (d) Sc
257. Which of the following is not a member of 3d-transition series?  
 (a) Fe (b) Co  
 (c) Au (d) Cu
258. Which is most soluble in water?  
 (a)  $\text{AgBr}$  (b)  $\text{AgCl}$   
 (c)  $\text{AgF}$  (d)  $\text{AgI}$
259. Addition of  $\text{SnCl}_2$  to  $\text{HgCl}_2$  give precipitate  
 (a) white turning to red  
 (b) white turning to grey  
 (c) black turning to white  
 (d) None of the above
260. The stability of ferric ion is due to  
 (a) half filled  $f$ -orbitals  
 (b) half filled  $d$ -orbitals  
 (c) completely filled  $f$ -orbitals  
 (d) completely filled  $d$ -orbitals
261. Which of the following lanthanide is commonly used?  
 (a) Lanthanum (b) Nobelium  
 (c) Thorium (d) Cerium
262.  $4\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{Heat}} 4\text{K}_2\text{CrO}_4 + 3\text{O}_2 + \text{X}$ ; in the above reaction X is  
 (a)  $\text{CrO}_3$  (b)  $\text{Cr}_2\text{O}_7$   
 (c)  $\text{Cr}_2\text{O}_3$  (d)  $\text{CrO}_5$
263. The colour of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  is  
 (a) blue (b) green  
 (c) white (d) red
264. Which of the following is most stable among  $\text{Cu}^+$ ,  $\text{Fe}^+$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ?  
 (a)  $\text{Cu}^+$  (b)  $\text{Fe}^+$   
 (c)  $\text{Fe}^{2+}$  (d)  $\text{Fe}^{3+}$
265. Brown glass and cement have, which element common in them?  
 (a) Fe (b) Al  
 (c) Na (d) All of these
266. The atomic size of cerium and promethium is quite close, due to  
 (a) they are in same period in Periodic Table  
 (b) they electronic configuration is same  
 (c)  $f$ -electrons have poor shielding effect  
 (d) nuclear charge is higher on cerium than promethium

267. The trivalent ion having largest size is  
 (a) Ti (b) Zr  
 (c) Hf (d) La
268. The transition metal used as a catalyst is  
 (a) nickel (b) platinum  
 (c) cobalt (d) all of these
269. Transition elements does not show  
 (a) paramagnetism (b) colour  
 (c) fixed valency (d) all of these
270. Aluminium appears like gold when mixed with  
 (a) 90% Cu (b) 75% Ni  
 (c) 80% Sn (d) 80% Co
271. Iron is dropped in very dil.  $\text{HNO}_3$ , it gives  
 (a) ferric nitrate  
 (b) ferric nitrate and  $\text{NO}_2$   
 (c) ferrous nitrate and ammonium nitrate  
 (d) ferrous nitrate and nitric oxide
272. Stainless steel contains  
 (a) Fe + Cr + Cu (b) Fe + C + Ni  
 (c) Fe + Cr + Ni (d) Fe + Ni + Cu
273. Which of the following alloys is used for making magnets for hearing aids?  
 (a) Alnico (b) German silver  
 (c) Invar (d) Monel metal
274. Cuprous ion is colourless while cupric ion is coloured because  
 (a) both have half-filled  $p$ - and  $d$ -orbitals  
 (b) both have unpaired electrons in  $d$ -orbitals  
 (c) cuprous ion has incomplete  $d$ -orbital and cupric ion has a complete  $d$ -orbital  
 (d) cuprous ion as a complete  $d$ -orbital and cupric ion has an incomplete  $d$ -orbital
275. Stainless steel does not rust because  
 (a) chromium and nickel combine with iron  
 (b) chromium forms an oxide layer and protects iron from rusting  
 (c) nickel present in it, does not rust  
 (d) iron forms a hard chemical compound with chromium present in it
276. Which of the following pairs of element cannot form an alloy?  
 (a) Zn, Cu (b) Fe, Hg  
 (c) Fe, C (d) Hg, Na
277. Which of the following types of metals form the most efficient catalysts?  
 (a) Alkali metals (b) Alkaline earth metals  
 (c) Transition metals (d) All of these
278. Impure metal forms volatile compound ( $X$ ) with CO and then ( $X$ ) gives pure metal on heating. Metal is  
 (a) Cu (b) Fe  
 (c) Ni (d) Pt
279. Which of the following chloride is water insoluble?  
 (a) HCl (b) AgCl  
 (c) Both (a) and (b) (d) None of these
280. Which of the following dissolves in hot conc. NaOH solution?  
 (a) Fe (b) Zn  
 (c) Cr (d) Ag
281. Reason of passivity of iron is  
 (a)  $\text{Fe}_2\text{O}_3$  (b)  $\text{Fe}_3\text{O}_4$   
 (c) FeO (d)  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
282. Which is wrongly matched?  
 (a) Duralumin — Al + Cu + Mg + Mn  
 (b) Alnico — Fe + Al + Ni + Cu  
 (c) German silver — Cu + Zn + Ni  
 (d) Monel metal — Cu + Zn + Sn
283. Formula of green vitriol oil is  
 (a)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (b)  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$   
 (c)  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (d)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
284. Which of the following is called white vitriol?  
 (a)  $\text{ZnCl}_2$  (b)  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$   
 (c)  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (d)  $\text{Al}_2(\text{SO}_4)_3$
285. Which of the following is not an actinide?  
 (a) Curium (b) Californium  
 (c) Uranium (d) Terbium
286. Europium is  
 (a)  $s$ -block element (b)  $p$ -block element  
 (c)  $d$ -block element (d)  $f$ -block element
287. Which of the following is not an actinoid?  
 (a) Am (b) Cm  
 (c) Fm (d) Tm
288. Most oxidising agent is  
 (a)  $[\text{WO}_4]^{2-}$  (b)  $[\text{CrO}_4]^{2-}$   
 (c)  $[\text{CeO}_4]^{2-}$  (d)  $[\text{MnO}_4]^{2-}$
289. Which of the following mixture is chromium acid?  
 (a)  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{HCl}$  (b)  $\text{K}_2\text{SO}_4 + \text{conc. H}_2\text{SO}_4$   
 (c)  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{conc. H}_2\text{SO}_4$  (d)  $\text{H}_2\text{SO}_4 + \text{HCl}$
290. In reduction of dichromate by Fe(II), the number of electrons involved per chromium atom is  
 (a) 2 (b) 3  
 (c) 4 (d) 1
291. Which alloy contains Cu, Sn and Zn?  
 (a) Gun metal (b) Solder  
 (c) Type metal (d) Bronze
292. Finely divided iron combines with CO to give  
 (a)  $\text{Fe}(\text{CO})_5$  (b)  $\text{Fe}_2(\text{CO})_9$   
 (c)  $\text{Fe}_2(\text{CO})_{12}$  (d)  $\text{Fe}(\text{CO})_6$
293. Green vitriol is formed by  
 (a)  $\text{FeS}_2 + \text{H}_2\text{O} + \text{O}_2$  (b)  $\text{FeS}_2 + \text{H}_2\text{O} + \text{CO}_2$   
 (c)  $\text{FeS}_2 + \text{CO} + \text{CO}_2$  (d)  $\text{FeS}_2 + \text{CO}$



294. Thermite is a mixture of  
 (a)  $\text{MgO} + \text{Al}$  (b)  $\text{Fe}_2\text{O}_3 + \text{Al}$   
 (c)  $\text{Zn} + \text{CaCO}_3$  (d)  $\text{Zn} + \text{P}_2\text{O}_5$
295. Which plays a major role in the formation of complex compound?  
 (a) Transition metal  
 (b) Lanthanides and actinides  
 (c) Representative elements  
 (d) *p*-block element

### One or More Than One Options Correct

1. When KCN is added to  $\text{CuSO}_4$  solution  
 (a) KCN acts as a reducing agent  
 (b) KCN acts as a complexing agent  
 (c) complex  $\text{K}_3[\text{Cu}(\text{CN})_4]$  is formed  
 (d) complex  $\text{K}_2[\text{Cu}(\text{CN})_4]$  is formed
2. Which will not give metal on heating?  
 (a)  $\text{Ag}_2\text{CO}_3$  (b)  $\text{ZnCO}_3$   
 (c)  $\text{HgO}$  (d)  $\text{CuO}$
3. Electron transfer from  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  to  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  is likely to occur *via*  
 (a) *d-d* transition  
 (b) inner sphere electron transfer  
 (c)  $\text{S}_\text{N}1$  mechanism  
 (d) outer sphere electron transfer

4. Pyrolusite is  $\text{MnO}_2$  used to prepare  $\text{KMnO}_4$ . Steps are



Steps I and II are

- (a) fuse with  $\text{KOH}$ /air, electrolytic oxidation  
 (b) fuse with  $\text{KOH}$ /air, electrolytic reduction  
 (c) fuse with conc.  $\text{HNO}_3$ /air, electrolytic reduction  
 (d) dissolve in  $\text{H}_2\text{O}$ , oxidation
5. Fe is made passive by  
 (a) dil.  $\text{H}_2\text{SO}_4$  (b) dil.  $\text{HCl}$   
 (c) aqua-regia (d) conc.  $\text{H}_2\text{SO}_4$
6.  $\text{N}_2$  gas can be obtained by heating  
 (a)  $(\text{NH}_4)_2\text{C}_2\text{O}_7$  (b)  $\text{NH}_4\text{NO}_2$   
 (c)  $\text{NH}_4\text{VO}_3$  (d)  $\text{NH}_4\text{NO}_3$
7. Which are correct statements about  $\text{KMnO}_4$ ?  
 (a) Its solution is unstable in acidic medium  
 (b) Its small quantity added to conc.  $\text{H}_2\text{SO}_4$ , a green coloured solution containing  $\text{MnO}_3^+$  ions is formed  
 (c)  $\text{MnO}_4^-$  changes to  $\text{Mn}^{2+}$  in basic solution  
 (d) It is self-indicator in  $\text{Fe}^{2+}$  or  $\text{C}_2\text{O}_4^{2-}$  titration
8. Which are correct statements?  
 (a) In less acidic solution  $\text{K}_2\text{C}_2\text{O}_7$  and  $\text{H}_2\text{O}_2$  gives violet coloured diamagnetic  $[\text{CrO}(\text{O}_2)(\text{OH})]^-$  ion  
 (b) In alkaline  $\text{H}_2\text{O}_2$ ,  $\text{K}_2\text{CrO}_8$  (with tetraperoxo species  $[\text{Cr}(\text{O}_2)_4]^{3-}$ ) is formed

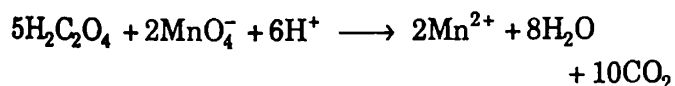
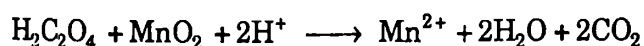
- (c) In ammoniacal solution,  $(\text{NH}_3)_3\text{CrO}_4$  is formed  
 (d)  $\text{CrO}_4^{2-}$  changes to  $\text{Cr}_2\text{O}_7^{2-}$  by oxidation

9. For  $\text{CrO}_3$  following is not true statement.  
 (a) It is called chromic acid  
 (b) It is colourless due to  $3d^0$  configuration  
 (c) It is bright orange solid and colour arises due to charge transfer  
 (d) It is toxic and corrosive
10. Lanthanoids are  
 (a) 14 elements in the sixth period (atomic no. = 90 to 103) that are filling *4f*-sublevel  
 (b) 14 elements in the seventh period (atomic no. = 90 to 103) that are filling *5f*-sublevel  
 (c) 14 elements in the sixth period (atomic no. = 58 to 71) that are filling *4f*-sublevel  
 (d) 14 elements in the seventh period (atomic no. = 58 to 71) that are filling *4f*-sublevel
11. When  $\text{CO}_2$  is passed into aqueous  
 (a)  $\text{Na}_2\text{CrO}_4$  solution, its yellow colour changes to orange  
 (b)  $\text{K}_2\text{MnO}_4$  solution, it disproportionates to  $\text{KMnO}_4$  and  $\text{MnO}_2$   
 (c)  $\text{Na}_2\text{Cr}_2\text{O}_7$  solution, its orange colour changes to green  
 (d)  $\text{KMnO}_4$  solution, its pink colour changes to green
12. Select incorrect statement(s).  
 (a) Nickel (II) compounds tend to be thermodynamically more stable than platinum (II)  
 (b) Platinum (IV) compounds are relatively more stable than nickel (IV) compounds  
 (c)  $\text{K}_2\text{Pt}^{\text{IV}}\text{Cl}_6$  exists  
 (d)  $\text{K}_2\text{Ni}^{\text{IV}}\text{Cl}_6$  exists
13. Standard reduction electrode potential at  $\text{Zn}^{2+}/\text{Zn}$  is  $-0.76$  V. This means  
 (a)  $\text{ZnO}$  is reduced to  $\text{Zn}$  by  $\text{H}_2$   
 (b)  $\text{Zn}$  liberates  $\text{H}_2$  with conc. acids  
 (c)  $\text{Zn}$  is generally the anode in an electrochemical cell  
 (d)  $\text{Zn}$  is generally the cathode in an electrochemical cell
14. Select correct statement(s) about  $[\text{CoCl}_6]^{4-}$  complex.  
 (a) It is paramagnetic  
 (b) It is a low-spin complex  
 (c) Oxidation number of cobalt is  $-4$   
 (d) The coordination number of cobalt is 6
15. Why does aqueous  $\text{Fe(III)}$  ion develop intense red colour when it reacts with  $\text{SCN}^-$  ion while  $\text{Fe(II)}$  ion does not?  
 (a)  $\text{Fe(III)}$  ion forms a charge transfer complex with  $\text{SCN}^-$  ions

- (b) Fe(III) is reduced to Fe(I) which is deep red in colour
- (c)  $\text{SCN}^-$  ion is oxidised to  $\text{CN}^-$  which forms red coloured complex with Fe(III) ion
- (d)  $\text{SCN}^-$  does not form any complex with Fe(III) ion
16. Select correct statement(s).
- (a) Stabilities of variable oxidation states can be explained by standard electrode potential
- (b)  $\text{Cr}^{2+}$  is unstable and  $\text{Cr}^{3+}$  is stable in aqueous solution
- (c)  $\text{Fe}^{2+}$  is stable and  $\text{Fe}^{3+}$  is unstable in aerated water
- (d) All of the above are correct statements
17. Select correct statement(s).
- (a) When  $\text{FeCl}_3$  solution is added to  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solution, in addition to  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$ ,  $\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]^-$  is also formed due to side redox reaction
- (b) When  $\text{FeCl}_2$  solution is added to  $\text{K}_3[\text{Fe}(\text{CN})_6]$  solution, in addition to  $\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$ ,  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$  is also formed due to side redox reaction
- (c)  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$  is paramagnetic while  $\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]^-$  is diamagnetic
- (d)  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$  is diamagnetic while  $\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]^-$  is paramagnetic

## Brain Twisters

1. A 0.81 g sample of pyrolusite ore (impure  $\text{MnO}_2$ ) is treated with 1.651 g of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ) in an acidic medium. Following this reaction the excess oxalic acid is titrated with 0.1 M  $\text{KMnO}_4$ , 30.6 mL being required. What is the % of  $\text{MnO}_2$  in the ore? ( $\text{Mn} = 55$ )



2. A steel sample is to be analysed for Cr and Mn simultaneously. By suitable treatment the Cr is oxidised to  $\text{Cr}_2\text{O}_7^{2-}$  and Mn to  $\text{MnO}_4^-$ . A 10.0 g of sample of steel is used to produce 250.0 mL of solution containing  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{MnO}_4^-$ . A 10.0 mL portion of this solution is added to a  $\text{BaCl}_2$  solution, and by proper adjusting the acidity, the Cr is precipitated as  $\text{BaCrO}_4$ ; 0.0549 g is obtained. A second 10 mL of the solution requires exactly 15.95 mL of 0.0750 M standard  $\text{Fe}^{2+}$  solution for its titration in acid solution. Calculate the % Mn and % Cr in the steel sample. ( $\text{Ba} = 137, \text{Cr} = 52, \text{Mn} = 55$ )

3. When a black powder (A) was heated strongly, it gave off a colourless non-inflammable gas. When (A) was boiled with excess dil.  $\text{H}_2\text{SO}_4$  and a little  $\text{H}_2\text{C}_2\text{O}_4$ , a non-inflammable odourless gas was evolved. The solution formed gave no precipitate when saturated with  $\text{H}_2\text{S}$ , but this saturated solution gave a light coloured precipitate when  $\text{NH}_4\text{OH}$  solution was added to it. A small sample of (A) was warmed with excess of conc.  $\text{HCl}$  and the gas liberated was passed into a conc.  $\text{KI}$  solution. This solution was made up to 200 mL; 20 mL of this solution was found to require 180 mL of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution iodometrically. Identify (A) and calculate the weight of (A) taken. Also write necessary reactions.

4. A monomeric compound of cobalt gives the following data on quantitative analysis :

$\text{Co}^{3+}$  : 21.24%  $\text{Cl}^-$  : 12.81%  $\text{NH}_3$  : 24.77%

$\text{SO}_4^{2-}$  : 34.65%  $\text{H}_2\text{O}$  : 6.53%

What is empirical formula of the complex?

5. One mole of the aqueous solution of the complex  $\text{CoCl}_3 \cdot 5\text{H}_2\text{O}$  when treated with excess of aqueous  $\text{AgNO}_3$  solution gave one mole of white precipitate of  $\text{AgCl}$ . What is the complex? (For this you should know that how many  $\text{Cl}^-$  ions are not coordinated to  $\text{Co}^{3+}$  — naturally one which is precipitated as  $\text{AgCl}$ )

6. For the following cell

|    |                         |                         |    |
|----|-------------------------|-------------------------|----|
|    | 0.005 M                 | 0.05 M                  |    |
| Hg | mercurous nitrate       | mercurous nitrate       | Hg |
|    | in 0.1 M $\text{HNO}_3$ | in 0.1 M $\text{HNO}_3$ |    |

EMF is 0.0295 V. What is charge on mercurous ion?

7. A solution made by dissolving 0.875 g of  $\text{Co}(\text{NH}_3)_4\text{Cl}_3$  in 25.0 g of water freezes at  $-0.56^\circ\text{C}$ . Calculate the number of moles of ions produced when 1 mole of  $\text{Co}(\text{NH}_3)_4\text{Cl}_3$  is dissolved in water, and suggest a structure for the complex ion present in the compound. Molal depression constant ( $K_f$ ) for water is  $1.86 \text{ K kg mol}^{-1}$  (molar mass of solute =  $235.5 \text{ g mol}^{-1}$ )

## Passage Comprehension Questions

### Passage 1

Read the following report from a science journal and answer the questions at the end of it.

CNIC (Commission on Nomenclature of Inorganic Chemistry) appointed by IUPAC in 1994, approved official names for elements with atomic number 104 to 109. With  $Z > 109$ , IUPAC recommended a nomenclature to be followed for naming these elements until their names are officially recognised. This nomenclature is based on the Latin words for the atomic numbers of the elements.

Very recently, on August 16, 2003, IUPAC approved the name for the superheavy element which was first produced in 1994.

- Atomic number of the recently discovered element is  
(a) 107 (b) 108  
(c) 109 (d) 110
- Name and symbol given to this new element is  
(a) Darmstadtium Ds  
(b) Bohrium Bh  
(c) Hassnium Hs  
(d) Meitnerium Mt
- IUPAC nomenclature of element with atomic number 110 is  
(a) Unu (b) Uun  
(c) Unn (d) Uum

### Passage 2

From the data given in the table, answer the following questions:

**Covalent Radii of the Transition Elements (pm)**

| K   | Ca  | Sc  | Ti  | V   | Cr  | Mn  | Fe  | Co  | Ni  | Cu  | Zn  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 203 | 174 | 144 | 132 | 122 | 117 | 117 | 117 | 116 | 115 | 117 | 125 |
|     |     |     | Zr  | Nb  |     |     |     |     |     |     |     |
|     |     |     | 145 | 134 |     |     |     |     |     |     |     |
|     |     |     | Hf  | Ta  |     |     |     |     |     |     |     |
|     |     |     | 144 | 134 |     |     |     |     |     |     |     |

- Atoms of the transition elements are smaller than those of the s-block elements. This is because of  
(a) usual contraction in size across a horizontal period  
(b) orbital electrons added to the penultimate *d*-shell rather than to the outer shell of the atom  
(c) both of the above  
(d) none of the above
- The radii of the elements from chromium ( $Z = 24$ ) to copper ( $Z = 29$ ) are very close to one another. This is due to  
(a) lanthanide contraction  
(b) the fact that successive addition of *d*-electrons screen the outer electrons (4s) from the inward pull of the nucleus  
(c) increase in radii due to increase in  $n$  is compensated by decrease in radii due to increase in  $Z$   
(d) all of the above

- From the table, atomic radii of Zr and Hf and those of Nb and Ta are same. It is due to  
(a) lanthanide contraction  
(b) the fact that increase in size due to increase in  $n$  is compensated by decrease in size due to increase in  $Z$  based on equation  $r_n = \frac{n^2 a_0}{Z}$   
(c) both of the above  
(d) none of the above

### Passage 3

Observe the following data and answer the questions at the end of it:

A characteristic property of the *d*-transition metals is their ability to exhibit several oxidation states. The stability of a given oxidation state depends on the nature of the element with which the transition metal is combined. The highest oxidation states are found in the compounds of fluorides and oxides because of most electronegative nature of F and O. The different oxidation states of 3*d*-series have been given below (very rare oxidation states are provided in parenthesis).

| Sc   | Ti   | V   | Cr  | Mn    | Fe   | Co   | Ni    | Cu    | Zn |
|------|------|-----|-----|-------|------|------|-------|-------|----|
|      |      |     | I   |       |      |      |       | I     |    |
| (II) | (II) | II  | II  | II    | II   | II   | II    | II    | II |
| III  | III  | III | III | (III) | III  | III  | (III) | (III) |    |
|      | IV   | IV  | IV  | IV    | (IV) | (IV) | (IV)  |       |    |
|      |      | V   | (V) | (V)   | (V)  | (V)  |       |       |    |
|      |      |     | VI  | VI    | VI   |      |       |       |    |
|      |      |     |     | VII   |      |      |       |       |    |

- Nickel also shows (0) oxidation state. This oxidation state is in  
(a) nitriles (b) carbonyls  
(c) cyclopentadienyl (d) in all of these
- These elements do not show the properties characteristic of transition elements  
(a) Fe, Co, Ni (b) Sc, Y, La  
(c) Cu, Ag, Au (d) Zn, Cd, Hg
- In which case(s) there is change in oxidation number?  
(a) aqueous solution of  $\text{CrO}_4^{2-}$  is acidified  
(b)  $\text{SO}_2$  gas is passed into  $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$   
(c)  $\text{Cr}_2\text{O}_7^{2-}$  solution is made alkaline  
(d)  $\text{CrO}_2\text{Cl}_2$  is dissolved in NaOH
- Most transition metals are inert towards acids or react slowly with them because of  
(a) negative standard reduction potential  
(b) protective layer of oxide  
(c) both of the above  
(d) none of the above

5. For Ni and Pt, different I.P. in MJ mol<sup>-1</sup> are given below:

|    | (IP) <sub>1</sub> + (IP) <sub>2</sub> | (IP) <sub>3</sub> + (IP) <sub>4</sub> |
|----|---------------------------------------|---------------------------------------|
| Ni | 2.49                                  | 8.80                                  |
| Pt | 2.60                                  | 6.70                                  |

hence

- (a) nickel (II) compounds tend to be thermodynamically more stable than platinum (II)  
 (b) platinum (IV) compounds tend to be more stable than nickel (IV)  
 (c) both (a) and (b)  
 (d) none of the above is correct
6. Match the compounds of column X with oxidation state of chromium in column Y.

| Column X                                              | Column Y |
|-------------------------------------------------------|----------|
| I [Cr(H <sub>2</sub> O) <sub>6</sub> ]Cl <sub>3</sub> | 5        |
| II CrO <sub>5</sub>                                   | 4        |
| III K <sub>3</sub> CrO <sub>8</sub>                   | 6        |
| IV (NH <sub>3</sub> ) <sub>3</sub> CrO <sub>4</sub>   | 3        |

| I     | II | III | IV |
|-------|----|-----|----|
| (a) 3 | 6  | 5   | 4  |
| (b) 3 | 4  | 5   | 6  |
| (c) 4 | 5  | 6   | 3  |
| (b) 6 | 5  | 4   | 3  |

### Passage 4

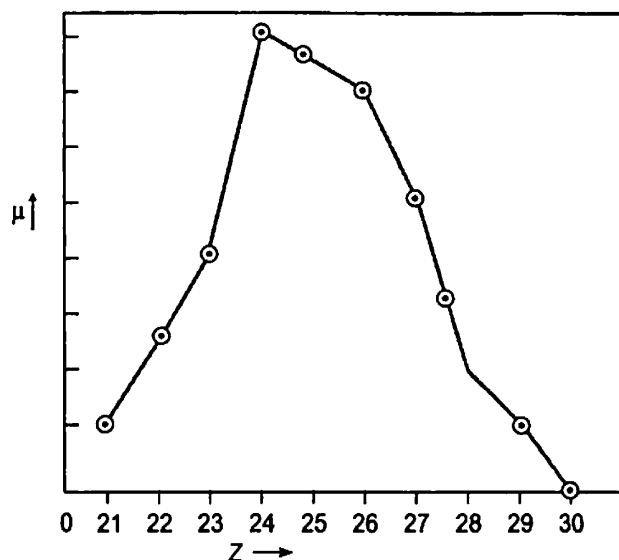
Read the following short write-up and answer the questions given:

"The transition elements have an unparalleled tendency to form coordination compounds with Lewis bases that is with groups which are able to donate an electron pair (called ligands)."

- The tendency to form complexes by transition metal compared to s and p-block elements is due to
  - their smaller size
  - higher nuclear charge
  - presence of low energy vacant orbitals to accept lone pair of electrons donated by ligands
  - all of the above
- Out of [Fe(CN)<sub>6</sub>]<sup>4-</sup>, [Ni(CN)<sub>4</sub>]<sup>2-</sup> and [Ni(CO)<sub>4</sub>]
  - all have identical geometry
  - all are paramagnetic
  - all are diamagnetic
  - [Fe(CN)<sub>6</sub>]<sup>4-</sup> is diamagnetic but [Ni(CN)<sub>4</sub>]<sup>2-</sup> and [Ni(CO)<sub>4</sub>] are paramagnetic

### Passage 5

Following diagram represents variation of magnetic moment ( $\mu$ ) with atomic number Z for 3d-series elements:



Magnetic moment of 3d-series elements (on arbitrary scale)

Based on this, answer the following questions.

- Consider following statements:
 

A : The magnetic moment arises from the spin and orbital motions. It is measured in the unit of BM.  
 B : Every coloured ion is paramagnetic and every paramagnetic ion is coloured.  
 C : Fe, Co and Ni exhibit ferromagnetism.  
 D : Magnetic moment of  $N$  unpaired electron is  $N(N+2)$

Select correct statements.

  - A, B
  - B, C
  - C, D
  - A, C
- Maximum magnetic moment is 6.93 for chromium. This means number of unpaired electrons is
  - 4
  - 5
  - 6
  - 7
- Magnetic moment of Fe<sup>3+</sup> ion is  $\sqrt{35}$ . Thus,  $x$ , number of unpaired ( $N$ ) electrons and its electronic configuration are
 

| $x$    | $N$ | $E-C$                                |
|--------|-----|--------------------------------------|
| (a) +3 | 5   | [Ar] 3d <sup>5</sup>                 |
| (b) +2 | 4   | [Ar] 3d <sup>6</sup>                 |
| (c) +1 | 3   | [Ar] 3d <sup>7</sup>                 |
| (d) 0  | 4   | [Ar] 3d <sup>5</sup> 4s <sup>1</sup> |
- The oxygen carrying pigment, oxy-haemocyanin, containing two copper ions is diamagnetic, because
  - the two copper ions are in +1 oxidation state
  - one of the copper ions is in +1 oxidation state and the other is in +2 oxidation state
  - there are strong anti-ferromagnetic interactions between the two copper ions
  - there are ferromagnetic interactions between the two copper ions

### Passage 6

Read the following passage and answer the questions given at the end of it:

Many ionic and covalent compounds of transition elements (and also inner transition elements) are coloured. In contrast, compounds of the *s*- and *p*-block elements are almost always white. Colour may arise from an entirely different cause in ions with **incomplete *d* or *f*-shells**. In a free isolated gaseous ions, the five *d*-orbitals are degenerate, that is, they are identical in energy. The surrounding groups, which can be solvent molecules in solution or ligands in a complex or other ions in a crystal lattice, affect the energy of some *d*-orbitals more than others. Thus, the *d*-orbitals are no longer degenerate and at their simplest they form two groups of orbitals of different energy.

1. Two sets of *d*-orbitals with different energies in an octahedral complex are

- (a)  $d_{z^2}$  and  $d_{x^2-y^2}$
- (b)  $d_{x^2-y^2}$  and  $d_{xy}$
- (c)  $d_{z^2}$ ,  $d_{x^2-y^2}$  and  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$
- (d)  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$

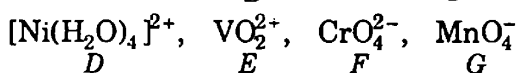
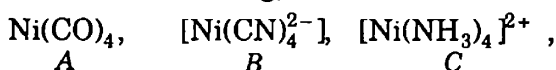
2. Consider following statements

- A : Colour of a transition metal complex is dependent on energy difference between two *d*-levels
- B : Colour of the complex is dependent on nature of the ligand and the type of complex formed
- C :  $\text{ZnSO}_4$  and  $\text{TiO}_2$  are white-in both *d*—*d*\* spectra are impossible

Select correct statements.

- (a) A, B, C
- (b) A, B
- (c) B, C
- (d) A, C

3. Out of the following, select colourless complexes



- (a) D, E
- (b) A, B, E
- (c) A, E
- (d) A, B

4.  $\text{MnO}_4^-$  is of intense pink colour, though Mn is in (+ 7) oxidation state. It is due to

- (a) oxygen gives colour to it
- (b) charge transfer when oxygen gives its electron to Mn making it Mn (+ VI) hence, coloured
- (c) charge transfer when Mn gives its electron to oxygen
- (d) none of the above is correct

5. Which is not true statement?

- (a) Ions of *d*-block elements are coloured due to *d*—*d* transition
- (b) Ions of *f*-block elements are coloured due to *f*—*f* transition
- (c)  $[\text{Sc(H}_2\text{O)}_6]^{3+}$ ,  $[\text{Ti(H}_2\text{O)}_6]^{4+}$  are coloured complexes
- (d)  $\text{Cu}^+$  is colourless ion

### Passage 7

Taking into account the following experimental facts answer the questions given at the end.

"When metallic copper is heated with concentrated sulphuric acid, in addition to copper(II) sulphate and sulphur dioxide, some copper (II) sulphide is also formed."

1. In which reaction,  $\text{SO}_2$  is formed?

- (a)  $\text{SO}_4^{2-} + 2e^- \longrightarrow$
- (b)  $\text{SO}_4^{2-} + 8e^- \longrightarrow$
- (c)  $\text{SO}_4^{2-} + 6e^- \longrightarrow$
- (d) in all of these

2. Copper (II) sulphide is formed because following side reaction is favourable due to its low solubility in acidic medium

- (a)  $\text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \longrightarrow$
- (b)  $\text{SO}_4^{2-} + 8\text{H}^+ + 8e^- \longrightarrow$
- (c) both of the above
- (d) none of the above

### Passage 8

Read the following short write-up and answer the questions given at the end.

Recent X-ray work, IR and other spectroscopic methods have proved that Turnbull's blue is identical to Prussian blue.

1. What is the common formula of Turnbull's blue and Prussian blue?

- (a)  $\text{Fe}_3[\text{Fe(CN)}_6]_2$
- (b)  $\text{Fe}_4[\text{Fe(CN)}_6]_3$
- (c)  $\text{KFe}[\text{Fe(CN)}_6]$
- (d)  $\text{KFe}_2[\text{Fe(CN)}_6]$

2. Intense blue colour arises as a result of

- (a) electron transfer between Fe(II) and Fe(I)
- (b) electron transfer between Fe(II) and Fe(III)
- (c) *d*—*d*\* transition
- (d) spin magnetic moment

### Passage 9

Based on the following statements answer the questions given at the end.

**Statement :** The mercurous ion is written as  $\text{Hg}_2^{2+}$  while the cuprous ion is written as  $\text{Cu}^+$ .

**Statement :**  $\text{Cu}^+$  is *d*<sup>10</sup> ion and colourless but  $\text{Cu}_2\text{O}$  is red and  $\text{Cu}_2\text{S}$  is black

1. Mercurous ion is written as  $\text{Hg}_2^{2+}$  because

- (a) magnetic moment of mercurous ion is zero and thus, 6s unpaired electron has been used in bonding to make  $\text{Hg}_2^{2+}$
- (b) in aqueous solution two  $\text{Hg}^+$  ions are solvated forming  $\text{Hg}_2^{2+}$
- (c)  $\text{HgCl}_2$  disproportionates to  $\text{Hg}_2\text{Cl}_2$  and  $\text{Hg}$
- (d) none of the above is correct

2. There is no *d*—*d*\* transition in  $\text{Cu}^+$ (I) ion, but  $\text{Cu}_2\text{O}$ (I) and  $\text{Cu}_2\text{S}$ (I) are coloured because of

- (a) presence of electronegative ions  $\text{O}^{2-}$ ,  $\text{S}^{2-}$

- (b) presence of divalent anions
- (c) charge transfer of electrons from  $O^{2-}$  or  $S^{2-}$  to the vacant orbitals of  $Cu^+$
- (d) all of the above

### Passage 10

Based on the following experimental facts answer the questions given at the end:

"Green solution of potassium manganate (VI), turns purple and a brown solid is precipitated when  $CO_2$  is bubbled into the solution".

- Purple colour is due to formation of
  - (a) manganese dioxide (IV)
  - (b) potassium permanganate (VII)
  - (c) manganese (II) ion
  - (d) none of the above
- Brown solid that is precipitated is of
  - (a) manganese dioxide (IV)
  - (b) potassium permanganate (VII)
  - (c) manganese oxide (II)
  - (d) manganese trioxide (III)
- Above change is observed when  $CO_2$  is passed into aqueous solution of the given ion. Function of  $CO_2$  is
  - (a) it makes solution acidic due to formation of  $H_2CO_3$
  - (b) it makes the solution basic due to formation of  $CO_3^{2-}$
  - (c) it is simply the medium of the reaction
  - (d) none of the above is correct
- Given experiment involves
  - (a) acid-base reaction
  - (b) a redox reaction
  - (c) disproportionation reaction
  - (d) decomposition reaction
- What happens when  $CO_2$  is passed into aqueous chromate (VI) solution
  - (a)  $CrO_3$  is formed
  - (b)  $CrO_5$  is formed
  - (c)  $Cr^{3+}$  is formed
  - (d)  $Cr_2O_7^{2-}$  is formed

### Passage 11

Read the following passage and answer the questions at the end of it.

When a piece of iron is dipped in conc.  $HNO_3$ , a slight reaction takes place which then ceases completely. There is no change in the appearance of the iron, but this does not displace Cu from  $CuSO_4$  solution which is however a common property of Fe. This behaviour is also observed with Cr and Al when in contact with  $HNO_3$ .

- Above phenomenon is called
  - (a) corrosion
  - (b) rusting
  - (c) passivity
  - (d) reduction

- When exposed to air and moisture, iron gets rapidly oxidised to
  - (a)  $FeO$
  - (b)  $Fe_2O_3 \cdot xH_2O$
  - (c)  $Fe_3O_4$
  - (d)  $FeO \cdot Fe_2O_3$

- Select some facts about passivity and corrosion (rusting) of iron:

A : Rusting is an electrochemical phenomenon  
 B : Passivity of iron prevents it from rusting  
 C : Passivity and rusting are reversible processes  
 Select correct statements.

- (a) A, B
- (b) B, C
- (c) A, C
- (d) A, B, C

### Passage 12

Based on the following qualitative test of chromium, answer the questions given at the end of it.

In qualitative analysis, a confirmatory test for chromium involves the formation of a blue transient peroxo species,  $CrO_5$ . It is formed when  $H_2O_2$  is added to an acidic solution containing  $Cr_2O_7^{2-}$ .

- Select correct statement about  $CrO_5$ .
  - (a) It has two types of oxygen-peroxide and oxide
  - (b) Oxidation number of Cr is +10
  - (c) It is formed by oxidation of  $Cr_2O_7^{2-}$
  - (d) All of the above are correct statements
- $CrO_5$  can be represented as
 

(a)

(b)

(c)

(d)
- When  $Cr_2O_7^{2-}$  is heated with  $Cl^-$  and conc.  $H_2SO_4$  deep red vapours of chromyl chloride are formed. Deep red vapours have formula
  - (a)  $CrOCl_2$
  - (b)  $(CrO)_2Cl_2$
  - (c)  $CrO_2Cl_2$
  - (d)  $CrO_3Cl$

### Passage 13

Read the following observation and answer the questions given at the end.

In an atmosphere with industrial smog, Cu corrodes to a basic sulphate  $Cu_2(OH)_2SO_4$  and basic carbonate  $Cu_2(OH)_2CO_3$ .

- Basic sulphate is generally formed during acid rain with a reaction
  - (a)  $2Cu + 2H_2O + SO_3 \longrightarrow Cu_2(OH)_2SO_4$
  - (b)  $2Cu + H_2O + SO_3 + O_2 \longrightarrow Cu_2(OH)_2SO_4$
  - (c)  $2Cu + H_2O + SO_2 + O_2 \longrightarrow Cu_2(OH)_2SO_4$
  - (d) all of the above

2. Formation of basic carbonate and basic sulphate involves some of the steps

A : a redox reaction

B : acid-base neutralisation reaction

C : precipitation reaction

D : decomposition

Select the steps actually taking place

(a) A, C, D

(b) B, C, D

(c) A, B, D

(d) A, B, C

3. This type of corrosion

(a) forms a tough adherent coating that protects the underlying metal

(b) causes loss of copper and thus the articles made of copper

(c) causes poisoning of the atmosphere

(d) gives a direct method of preparing basic copper carbonate and basic copper sulphate

## Assertion & Reason

Codes :

(a) Both A and R are true and R is the correct explanation of A.

(b) Both A and R are true but R is not the correct explanation of A.

(c) A is true but R is false.

(d) A is false but R is true.

(e) A and R both are false.

1. **Assertion (A)** : Most of the compounds of the transition elements are coloured in the solid and solution state.

**Reason (R)** : During  $d-d$  transition the  $d$ -electrons absorb certain radiation from the visible region of the spectrum.

2. **Assertion (A)** : The purple colour of  $\text{KMnO}_4$  is due to the charge transfer transition.

**Reason (R)** : The intense colour, in most of the transition metal complexes is due to  $d-d$  transition.

3. **Assertion (A)** : Nickel (II) compounds tend to be thermodynamically more stable than platinum (II).

**Reason (R)** : Platinum (IV) compounds are relatively more stable than nickel (IV) compounds.

4. **Assertion (A)** : Chromium can be used as a protective and non-corrosive plating on other metals.

**Reason (R)** : Due to atmospheric oxidation, chemically a inert layer of  $\text{Cr}_2\text{O}_3$  is formed.

5. **Assertion (A)** :  $[\text{Fe}(\text{CN})_6]^{3-}$  is more stable than  $[\text{Fe}(\text{CN})_6]^{4-}$ .

**Reason (R)** : Complexes where the iron is in the (III) oxidation state are more stable than those in (II) oxidation state.

6. **Assertion (A)** : Ionic radii of Ta and Nb are same.

**Reason (R)** : The lanthanide contraction cancels almost exactly the normal size increase on descending a group of transition elements.

7. **Assertion (A)** : Aqueous solution of  $\text{ZnO}$  is purely basic in nature.

**Reason (R)** :  $\text{ZnO}$  cannot be dissolved in dil. acid

8. **Assertion (A)** :  $\text{CrO}_3$  is an acidic oxide.

**Reason (R)** :  $\text{CrO}_3$  liberates  $\text{CO}_2$  with  $\text{Na}_2\text{CO}_3$ .

9. **Assertion (A)** : When  $\text{CrO}_3$  is dissolved in  $\text{NaOH}$ ,  $\text{CrO}_3$  goes in the cationic part.

**Reason (R)** :  $\text{Na}_2\text{CrO}_4$  (yellow) is formed.

10. **Assertion (A)** :  $\text{Cu}^{2+}(\text{aq})$  and  $\text{Cd}^{2+}(\text{aq})$  both form stable complexes with  $\text{CN}^-(\text{aq})$ .

**Reason (R)** :  $[\text{Cu}(\text{CN})_4]^{3-}$  is not decomposed by  $\text{H}_2\text{S}$ .

11. **Assertion (A)** : Green solution of potassium manganate (VI),  $\text{K}_2\text{MnO}_4$  turns purple and brown solid is precipitated when  $\text{CO}_2$  is bubbled into it.

**Reason (R)** :  $\text{K}_2\text{MnO}_4$  changes to  $\text{K}_3\text{MnO}_8$  by  $\text{CO}_2$ .

12. **Assertion (A)** : Prussian blue and Turnbull's blue are formed by different reagents, yet they are identical.

**Reason (R)** : They have formula as  $\text{Fe}[\text{Fe}(\text{CN})_6]^\cdot$ .

13. **Assertion (A)** : Copper(I) chloride is white, white  $\text{Cu(I)}$  oxide is red.

**Reason (R)** : In  $\text{Cu(I)}$  oxide, crystal structure has excess copper (I) ions making it defective.

## True & False

1. On heating  $\text{MnO}_2$  with  $\text{Fe}_2\text{O}_3$  and carbon ferromanganese is formed.

2. Zn reduces  $\text{VO}^{2+}$  to  $\text{V}^{3+}$  in acidic medium.

3.  $\text{Cu}^+$  and  $\text{Hg}_2^{2+}$  both are paramagnetic.

4.  $\text{ZnO}$  is yellow when hot, but white when cold.

5. When  $\text{KCN}$  is added to  $\text{CuSO}_4$  solution, a stable complex  $\text{K}_3[\text{Cu}(\text{CN})_4]$  is formed.

6. Cast iron is the purest form of iron.

7. When excess of  $\text{AgNO}_3$  solution is added to 1 mol of  $\text{aq. FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 2 mol of  $\text{AgCl}$  is formed.

8. Aqueous solution of  $\text{CO}_2$  changes  $\text{CrO}_4^{2-}$  (yellow) into  $\text{Cr}_2\text{O}_7^{2-}$  (orange).

9. Chromium and iron are made passive (inert) by  $\text{HNO}_3$ .

10. Due to lanthanide contraction, Zr and Hf have equal size.
11. Oxidation state of Cr in  $\text{CrO}_5$  is +10.
12. Maximum oxidation state of osmium is +6.
13. In  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ , magnetic moment of Fe is  $\sqrt{15}$  BM.
14. Equivalent weight of  $\text{MnO}_4^-$  in acidic medium is one-fifth of the molecular weight.
15. Stains of blue ink on the cloth can be removed by oxalic acid.
16. When  $\text{H}_2\text{S}$  gas is passed into  $\text{K}_2[\text{Cd}(\text{CN})_4]$ , no ppt. is found since  $\text{Cd}^{2+}$  is in the complex form.
17. When  $\text{H}_2\text{S}$  gas is passed into aqueous  $\text{ZnCl}_2$  solution, white ppt. of  $\text{ZnS}$  are formed.
18.  $\text{MnO}_4^-$  has Mn in +7 state thus it is colourless due to no unpaired electron in  $d$ -orbital.
19. Nickel(II) compounds tend to be thermodynamically more stable than platinum(II) while platinum (IV) compounds are relatively more stable than nickel(IV).
20.  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  have same magnetic moment and identical structure.
21. The colour of the  $d$ -block ions is due to  $d-d^*$  transition.
22.  $\text{ZnSO}_4$  and  $\text{TiO}_2$  are colourless (white) due to absence of  $d-d^*$  transition.
23.  $\text{CrO}_3$  is also called chromic acid.
24.  $\text{KMnO}_4$  solution is used as a primary standard solution in volumetric titration.
25. Mohr's salt is isomorphous with white vitriol and epsom salt.
26. Correct formula of blue vitriol is  $[\text{Cu}(\text{H}_2\text{O})_5]\text{SO}_4$ .
27.  $\text{Hg}_2\text{Cl}_2$  is blackened by addition of aq.  $\text{NH}_3$  due to formation of  $[\text{Hg}_2(\text{NH}_3)_2]\text{Cl}_2$ .
28.  $\text{HgCl}_2$  is soluble in excess of KI due to formation of  $\text{K}_2\text{HgI}_4$ .
29.  $\text{HgCl}_2$  is called calomel and  $\text{Hg}_2\text{Cl}_2$  is called corrosive sublimate.
30. Solution of  $\text{Al}(\text{C}_2\text{H}_5)_3$  and  $\text{TiCl}_4$  in cyclohexane react to form Ziegler-Natta catalyst.
31.  $\text{AgBr}$  is insoluble in  $\text{Na}_2\text{S}_2\text{O}_3$  due to formation of white precipitate of  $\text{Ag}_2\text{S}_2\text{O}_3$ .
32. The element (Unn) has atomic number of 100.
33. The actinoids are more electropositive and are reactive, reactivity increases with increase in atomic number.

34. Maximum oxidation state of Np is +6.

35. When  $\text{CrO}_2\text{Cl}_2$  is dissolved in  $\text{NaOH}$ , yellow colour is due to the anion.

## Fill in the Blanks

1. Coagulation of blood takes place by use of ..... solution.
2. Rust stains can be removed by using ..... which forms water soluble complex with ..... ion of rust.
3. Mercurous ion is ..... and cuprous ion is ..... (magnetic behaviour).
4. 'Brown ring' in ring test of nitrate is due to the formation of  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  in which magnetic moment is found to be ..... BM due to presence of ..... unpaired electrons.
5. In 'ring test', NO transfers its electron to  $\text{Fe}^{2+}$  (charge transfer) thus there are ..... and ..... ions in  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ .
6. Measurement of magnetic moment ( $\sqrt{8}$  BM) of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$  indicates that Fe is ..... state and NO exists as .....
7.  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  differ in their ..... while their structures are similar.
8.  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Ni}(\text{CO})_4]$  are ..... but  $[\text{Ni}(\text{CN})_4]^{2-}$  is ..... and  $[\text{Ni}(\text{CO})_4]$  is tetrahedral in structure.
9. Titanium is called the ..... metal.
10. Rusting of iron is a special case of .....
11. In case of  $\text{Cu}^+$ , all the  $d^{10}$  electrons are paired, hence it is ..... and it does not give ..... transition.
12. In  $\text{MnO}_4^-$ , Mn is in +7 state with  $d^0$  electronic configuration but it is coloured ion due to ..... from ..... to .....
13. Due to charge transfer from  $\text{O}^{2-}$  to Mn(VII), O is ..... and Mn(VII) changes to ..... hence  $\text{MnO}_4^-$  is .....
14. Magnetic moment of  $\text{Fe}^{2+}$  (24 electrons) is ..... and is thus ..... than Cr that of (24 electrons).
15.  $\text{FeO}$  is a ..... compound and is ..... deficient.
16. Fe, Co and Ni have approximately ..... size.
17. Due to ..... Zr and Hf, and also Nb and Ta have equal size.



18.  $V_2O_5$  is used as catalyst in ..... process for the manufacture of .....
19.  $[Fe(H_2O)_6]^{3+}$  reacts with  $H_2O$  forming ..... and  $H_3O^+$  and is thus ..... in nature.
20. .... is used to make many ferrous alloys including stainless and hard chromium steel.
21.  $Fe^{2+}$  salts can be determined volumetrically using ..... and ..... in acidic medium.
22.  $Cr_2O_7^{2-}/H^+$  and  $H_2O_2$  gives a deep blue-violet compound ..... in which oxidation number of Cr is .....
23. Oxidation number of Cr in  $K_2CrO_8$  with  $[Cr(O_2)_4]^{3-}$  ion is .....
24. In  $(NH_3)_3CrO_4$ , oxidation number of Cr is +4 hence, it is .....
25. Chromyl ion is .....
26.  $(NH_4)_2Cr_2O_7$  (orange) changes to green due to formation of ..... by ..... and ..... gas is obtained by .....
27.  $MoO_3$  and  $CrO_3$  are strongly ..... hence dissolve in .....
28.  $CrO_4^{2-}$  changes to  $Cr_2O_7^{2-}$  in ..... solution and  $Cr_2O_7^{2-}$  changes to  $CrO_4^{2-}$  in ..... solution.
29.  $Mn^{3+}$  disproportionates in  $H_2O/H^+$  to ..... and .....
30. In acidic medium, equivalent weight of  $MnO_4^-$  is ..... of molecular weight and in dilute alkaline medium it is ..... of molecular weight.
31. When  $CO_2$  gas is passed into  $K_2MnO_4$  solution, there is formation of ..... and ..... by .....
32. CO is toxic since when inhaled, it forms complex with ..... of ..... present in blood.
33. When a small amount of  $KMnO_4$  is added to conc.  $H_2SO_4$ , a green solution containing ..... ion is formed.
34. When excess of  $KMnO_4$  is added to conc.  $H_2SO_4$ , an explosive oil ..... is formed.
35.  $Fe(OH)_2$  dissolves in concentrated solution of NaOH forming a blue-green complex .....
36. Turnbull's blue and Prussian blue are identical with formula .....

37.  $Fe_3O_4$  is a ..... oxide .....
38.  $NaFeO_2$  on hydrolysis gives ..... and .....
39. Fehling solution contains ..... and sodium potassium tartrate (Rochelle salt).
40.  $CuSO_4$  is determined iodometrically by its reactions with ..... and then titration with ..... solution.

## Matrix-Match Type Questions

### I. Only One Correct

1. Match the alloys (in List I) with the constituents metal (in List II).

| List I           | List II       |
|------------------|---------------|
| A. Gun metal     | 1. Pb, Sn     |
| B. German silver | 2. Cu, Sn, Zn |
| C. Brass         | 3. Cu, Zn     |
| D. Solder        | 4. Cu, Zn, Ni |

2. Match the natural coordination compounds (in List I) with metals therein (in List II).

| List I                | List II |
|-----------------------|---------|
| A. Nitrogenases       | 1. Cu   |
| B. Cytochrome oxidase | 2. Mo   |
| C. Cytochrome C       | 3. Zn   |
| D. Carboxy peptidase  | 4. Fe   |

3. Match the lanthanide ions ( $Ln^{3+}$ , in List I) with their calculated magnetic moments (in List II).

| List I       | List II    |
|--------------|------------|
| A. $Ce^{3+}$ | 1. 7.94 BM |
| B. $Nd^{3+}$ | 2. 4.90 BM |
| C. $Gd^{3+}$ | 3. 1.73 BM |
| D. $Pm^{3+}$ | 4. 3.87 BM |

4. Match the catalysts in List I with their uses in List II.

| List I      | List II                                               |
|-------------|-------------------------------------------------------|
| A. $TiCl_4$ | 1. Adams catalyst in reduction                        |
| B. $PdCl_2$ | 2. In preparation of $(CH_3)_2SiCl_2$                 |
| C. $Pt/PtO$ | 3. Reppe synthesis                                    |
| D. Cu       | 4. Used as the Natta catalyst in polythene production |
| E. Ni       | 5. Wake process for converting $C_2H_4$ to $CH_3CHO$  |

5. Match the alloys (in List I) with their constituents (in List II).

| List I           | List II                     |
|------------------|-----------------------------|
| A. Invar         | 1. 70% Cu + 30% Zn          |
| B. Brass         | 2. 66% Ni + 33% Cu          |
| C. Monel         | 3. 36% Ni                   |
| D. Coinage metal | 4. 60% Ni + 20% Fe + 20% Cr |
| E. Nichrome      | 5. 75% Cu + 25% Ni          |

6. Match the compounds of List I with oxidation state of List II.

| List I                                            | List II |
|---------------------------------------------------|---------|
| A. $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ | 1. 5    |
| B. $\text{CrO}_5$                                 | 2. 4    |
| C. $\text{K}_3\text{CrO}_8$                       | 3. 6    |
| D. $(\text{NH}_3)_3\text{CrO}_4$                  | 4. 3    |

7. Match the compounds in List I with their uses in List II.

| List I                      | List II                           |
|-----------------------------|-----------------------------------|
| A. $\text{Hg}_2\text{Cl}_2$ | 1. Metallurgical extraction of Ag |
| B. $\text{ZnO}$             | 2. Electrode                      |
| C. $\text{ZnSO}_4$          | 3. Luminous paints                |
| D. $\text{Zn}$              | 4. Lithophone                     |

8. Match the underlined atoms in List I with oxidation number in List II.

| List I                                                | List II |
|-------------------------------------------------------|---------|
| A. <u>Mn</u> $\text{O}_4^-$                           | 1. 1    |
| B. <u>Cr</u> $\text{O}_4^{2-}$                        | 2. 2    |
| C. <u>Fe</u> $[\text{Fe}^{\text{II}}(\text{CN})_6]^-$ | 3. 3    |
| D. <u>Zn</u> $\text{O}_2^{2-}$                        | 4. 6    |
| E. <u>Ag</u> $(\text{CN})_2^-$                        | 5. 7    |

9. Match the alloys (in List I) with their constituents (in List II).

| List I           | List II                      |
|------------------|------------------------------|
| A. Invar         | 1. 70% Cu + 30% Zn           |
| B. Brass         | 2. 66% Ni + 33% Cu           |
| C. Monel         | 3. 36% Ni                    |
| D. Coinage metal | 4. 60% Ni + 20% Fe + 20% Cr. |
| E. Nicrome       | 5. 75% Cu + 25% Ni           |

10. Match catalyst is (List I) according to its name and function.

| List I Catalyst                         | List II Name        | List III Function                                      |
|-----------------------------------------|---------------------|--------------------------------------------------------|
| A. $\text{TiCl}_4$                      | 1. Fenton's reagent | P. Oxidation of alcohol                                |
| B. $\text{FeSO}_4/\text{H}_2\text{O}_2$ | 2. Ziegler-Natta    | Q. Polythene preparation                               |
| C. $\text{Pd/C}$                        | 3. Lindlar          | R. Hydrogenation of alkynes to give <i>cis</i> -alkene |
| D. $\text{Pt/PtO}$                      | 4. Adam             | S. Synthesis of $\text{CH}_3\text{OH}$                 |

11. Match the complex ion (List I) with its spin-only spin-only magnetic moment (List II).

| List I                                      | List II    |
|---------------------------------------------|------------|
| A. $[\text{Co}(\text{NH}_3)_6]^{3+}$        | 1. 1.73 BM |
| B. $[\text{Fe}(\text{CN})_6]^{3-}$          | 2. 5.92 BM |
| C. $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ | 3. 0.0 BM  |
| D. $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ | 4. 2.83 BM |

## II. One or More Correct

1. Match the species in Column I that can react (oxidise, reduce, give ppt) species in Column II.

| Column I                       | Column II                          |
|--------------------------------|------------------------------------|
| A. $\text{Fe}^{2+}$            | 1. $\text{Cr}_2\text{O}_7^{2-}$    |
| B. $\text{C}_2\text{O}_4^{2-}$ | 2. $\text{CrO}_4^{2-}$             |
| C. $\text{Pb}^{2+}$            | 3. $[\text{Fe}(\text{CN})_6]^{3-}$ |
| D. $\text{Ag}^+$               | 4. $\text{MnO}_4^-$                |
| E. $\text{SO}_2$               | 5. $\text{S}_2\text{O}_3^{2-}$     |

2. Match the species in Column I with their characteristics in Column II.

| Column I              | Column II                     |
|-----------------------|-------------------------------|
| A. $\text{Cu}^+$      | 1. Paramagnetic               |
| B. $\text{Cu}^{2+}$   | 2. Diamagnetic                |
| C. $\text{Hg}^{2+}$   | 3. Corrosive sublimate        |
| D. $\text{Hg}_2^{2+}$ | 4. Calomel                    |
| E. $\text{Zn}^{2+}$   | 5. Colour with $\text{SCN}^-$ |
|                       | 6. $d^{10}$                   |
|                       | 7. Reacts with KI             |

## Integer Answer Types

This section contains 9 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the ORS have to be darkened. For example, if the correct answers to question number X, Y, Z and W (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will like the following.

| X | Y | Z | W |
|---|---|---|---|
| Ⓐ | Ⓐ | Ⓐ | Ⓐ |
| Ⓑ | Ⓑ | Ⓑ | Ⓑ |
| Ⓒ | Ⓒ | Ⓒ | Ⓒ |
| Ⓓ | Ⓓ | Ⓓ | Ⓓ |
| Ⓔ | Ⓔ | Ⓔ | Ⓔ |
| Ⓕ | Ⓕ | Ⓕ | Ⓕ |
| Ⓖ | Ⓖ | Ⓖ | Ⓖ |
| Ⓗ | Ⓗ | Ⓗ | Ⓗ |
| Ⓘ | Ⓘ | Ⓘ | Ⓘ |

Answer of this integer type question are in the form of colours given in number.

- |           |                       |
|-----------|-----------------------|
| 1. Violet | 6. Orange             |
| 2. Indigo | 7. Red                |
| 3. Blue   | 8. Prussian blue      |
| 4. Green  | 9. Cherry Red         |
| 5. Yellow | 0. Colourless (white) |
- Colour of the

### Set I

- Complex when KCNS is added to  $\text{FeCl}_3$  solution.
- Complex when  $\text{NH}_3$  is added to  $\text{CuSO}_4$  solution.
- Compounds when  $\text{K}_2\text{Cr}_2\text{O}_7$  solution is made alkaline.
- Compound when  $\text{K}_2\text{CrO}_4$  solution is made acidic.
- Compound when  $\text{Cl}_2$  gas is passed into  $\text{K}_2\text{MnO}_4$  solution.
- Compound when  $\text{SO}_2$  gas is passed into acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.
- Compound when  $\text{CuSO}_4$  is treated with KI and then titrated with  $\text{Na}_2\text{S}_2\text{O}_3$  solution.
- Complex when dimethyl-glyoxime (in alcohol) added to ammoniacal nickel chloride solution.
- Complex when  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is added to  $\text{FeCl}_3$  solution.

### Set II

This section contains 8 questions

- $\text{Fe}^{2+}$  (24 electrons) has ..... electrons in 3d-orbitals.

- $\text{Cr}^+$  (23 electrons) has ..... electrons in  $(n-1)$  orbitals.
- Maximum oxidation state shown by manganese is .....
- Magnetic moment of Mn in  $\text{MnSO}_4$  is 5.91 BM. Thus it has ..... electrons in 3d-orbitals.
- $\text{CrO}_5$  has ..... peroxy linkage(s).
- 2.674 g of  $\text{CoCl}_3 \cdot 6\text{NH}_3$  (molar mass =  $267.4 \text{ g mol}^{-1}$ ) in aqueous solution gave 4.305 g of white precipitate of  $\text{AgCl}$  (molar mass =  $143.5 \text{ g mol}^{-1}$ ). On reaction with excess of  $\text{AgNO}_3$  solution. Thus Cl atoms in outer sphere of the complex is .....
- Number of oxygen atom(s) between two chromium atoms in  $\text{Cr}_2\text{O}_7^{2-}$  is .....
- When  $\text{CrO}_5$  is treated with  $\text{H}_2\text{O}_2$  and KOH, a red-brown compound  $\text{K}_3[\text{Cr}(\text{O})_x]$  is formed.  $x$  is .....

### Set III

This section contains 8 questions

- 2.78 g of  $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$  on treatment with excess of  $\text{BaCl}_2$  solution gives 2.33 g of white precipitate of  $\text{BaSO}_4$ . What is value of  $x$ ? (Ba = 137, S = 32, Fe = 56, O = 16)
- How many of the following also forms dimer?  $\text{NO}_2$ ,  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{CuSO}_4$ ,  $\text{PCl}_3$
- How many of the following are paramagnetic as well as coloured species?  $\text{O}_2$ ,  $\text{NO}_2$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$
- What is van't Hoff factor of  $\text{Hg}_2(\text{NO}_2)_2$  if it is 100% ionised in aqueous solution?
- How many of the following have underlined atoms in different oxidation states?  $\text{Hg}\underline{\text{I}}_4^{2-}$ ,  $\text{S}_2\underline{\text{O}}_3^{2-}$ ,  $\text{S}_4\underline{\text{O}}_6^{2-}$ ,  $\text{Cr}\underline{\text{O}}_5$ ,  $\text{Fe}_3\underline{\text{O}}_4$ ,  $\text{Pb}_3\underline{\text{O}}_4$
- How many of the following pairs have approximately equal radii  $(\text{Zr}, \text{Hf})$ ,  $(\text{Nb}, \text{Ta})$ ,  $(\text{Cr}, \text{Mn})$ ,  $(\text{Mn}, \text{Fe})$ ,  $(\text{Nb}^{3+}, \text{Ta}^{3+})$ ,  $(\text{Zr}^{4+}, \text{Hf}^{4+})$
- How many of the following are amphoteric?  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{VO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_3$
- How many  $\text{H}_2\text{O}$  molecules are in coordination sphere in  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$

## Test Yourself on the Periodic Table

1. Locate with each of the following electron configuration on the Periodic Table given the transition elements. Identify each element.

- (a)  $[\text{Ar}] 3d^7 4s^2$       (b)  $[\text{Ar}] 3d^5 4s^1$   
 (c)  $[\text{Kr}] 4d^2 5s^2$       (d)  $[\text{Xe}] 4f^3 6s^2$

2. Locate the transition elements, on the Periodic Table, with following specifications :

- (a) Element in 3d series giving +7 oxidation state  
 (b) Element in 5th period whose divalent cation has  $d^{10}$  configuration  
 (c) Element which has been recently named as Ds  
 (d) Elements which forms colourless ion in  $M^+$  state

3. Locate the period, group and block of the element Ds recently named by IUPAC. Also write its electronic configuration.

4. On the Periodic Table locate

- (1) Coinage metals      (2) Lanthanides  
 (3) Actinides      (4) Alkaline earth elements  
 (5) Chalcogens

5. On the Periodic Table, locate the elements

- (a) in 3d series which form insoluble sulphides  
 (b) in 4d series which form insoluble sulphides  
 (c) with  $s^2 p^6$  configuration of valence shell  
 (d) with  $[\text{Ar}]$  configuration in +3 state

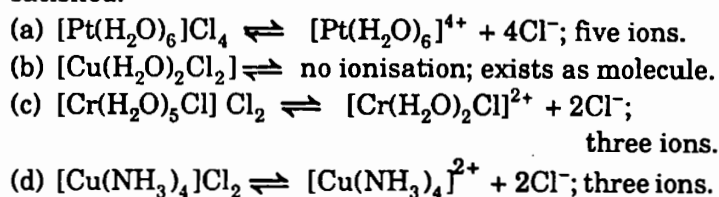
# Answers & Solutions

## Master Exercises

### Exercise 1

#### Short Answer Type Questions

1. In all cases CN of the metal [Cu = 4, Cr = 6, Pt = 6] is to be satisfied.



| 2. Ion ( $M^{2+}$ ) | Z  | Electrons ( $M^{2+}$ ) | EC ( $M^{2+}$ ) | Unpaired electron | Magnetic moment (BM) |
|---------------------|----|------------------------|-----------------|-------------------|----------------------|
| $\text{Sc}^{2+}$    | 21 | 19                     | $3d^1$          | 1                 | $\sqrt{3}$           |
| $\text{Ti}^{2+}$    | 22 | 20                     | $3d^2$          | 2                 | $\sqrt{8}$           |
| $\text{V}^{2+}$     | 23 | 21                     | $3d^3$          | 3                 | $\sqrt{15}$          |
| $\text{Cr}^{2+}$    | 24 | 22                     | $3d^4$          | 4                 | $\sqrt{24}$          |
| $\text{Mn}^{2+}$    | 25 | 23                     | $3d^5$          | 5                 | $\sqrt{35}$          |
| $\text{Fe}^{2+}$    | 26 | 24                     | $3d^6$          | 4                 | $\sqrt{24}$          |
| $\text{Co}^{2+}$    | 27 | 25                     | $3d^7$          | 3                 | $\sqrt{15}$          |
| $\text{Ni}^{2+}$    | 28 | 26                     | $3d^8$          | 2                 | $\sqrt{8}$           |
| $\text{Cu}^{2+}$    | 29 | 27                     | $3d^9$          | 1                 | $\sqrt{3}$           |
| $\text{Zn}^{2+}$    | 30 | 28                     | $3d^{10}$       | 0                 | 0                    |

$$\text{Zn}^{2+} < \text{Sc}^{2+} = \text{Cu}^{2+} < \text{Ti}^{2+} = \text{Ni}^{2+} < \text{V}^{2+} = \text{Co}^{2+} < \text{Cr}^{2+} = \text{Fe}^{2+} < \text{Mn}^{2+}$$

3.  $[\text{Fe}(\text{CN})_6]^{4-}$  —  $d^2sp^3$  hybridised  $\text{Fe}^{2+}$  has all the paired electrons hence magnetic moment = zero.

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  —  $sp^3d^2$  hybridised  $\text{Fe}^{2+}$  has four unpaired electrons, hence magnetic moment =  $\sqrt{24}$  BM

4.  $[\text{Fe}(\text{CN})_6]^{4-}$  unpaired electron ( $N$ ) = 0,

$$\mu = \sqrt{N(N+2)} \text{ BM} = 0$$

$$[\text{Fe}(\text{CN})_6]^{3-} \quad N=1 \quad = \sqrt{3}$$

$$[\text{Ni}(\text{CN})_4]^{2-} \quad N=0 \quad = 0$$

$$[\text{Ni}(\text{H}_2\text{O})_4]^{2+} \quad N=2 \quad = \sqrt{8}$$

5.  $\sqrt{N(N+2)} = \sqrt{35} \Rightarrow N=5$  (unpaired electrons)

$$\Rightarrow x=3 (\text{Fe}^{3+})$$

$$\text{Fe}^{3+} = [\text{Ar}]3d^5$$

6. The  $s$ - and  $p$ - block elements do not have a partially filled  $d$ -shell so there cannot be any  $d-d^*$  transition. The energy to promote an  $s$ - or  $p$ - electron to a higher energy

level is much greater and corresponds to ultraviolet light being absorbed. Thus compound will not be coloured.

7. Colourless — (a), (b) (d), (i), (j) Coloured — (c), (e), (f), (g), (h).

8. (a), (b) — colourless (c), (d) — coloured.

9.  $\text{Hg}^{2+}$  has all filled  $5d$ -orbitals (no unpaired electron in  $5d$ ), hence no  $d-d^*$  transition, hence colourless.

10.  $\text{NO}_2$  — coloured and paramagnetic

$\text{Cu}^+$  — colourless

$\text{O}_2$  — paramagnetic

$\text{O}_3$  — diamagnetic

$\text{Hg}_2^{2+}$  — colourless

$\text{Cd}^{2+}$  — colourless

$\text{Al}$  — paramagnetic

$\text{C}$  (graphite) — paramagnetic.

11.  $\text{Sc}(21) : [\text{Ar}]3d^1 4s^2$

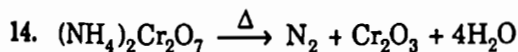
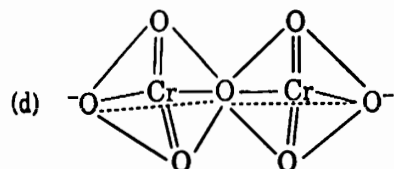
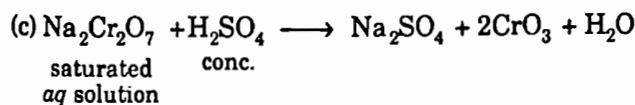
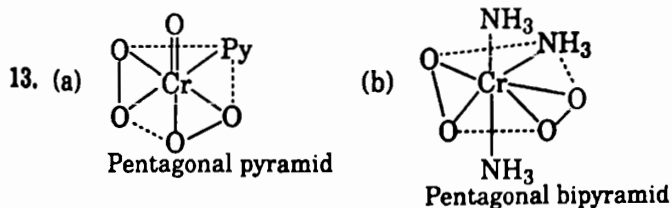
$\text{Sc}^{3+} : [\text{Ar}]3d^0$  no unpaired electron in  $d$ -orbital hence no ( $d-d^*$ ) transition hence colourless

$\text{Ti}(22) : [\text{Ar}]3d^2 4s^2$

$\text{Ti}^{3+} : [\text{Ar}]3d^1$  due to unpaired electron in  $d$ -orbital ( $d-d^*$ ) transition possible hence coloured.

12. A. (a) Nb = Ta (b) Cr = Mn  
 (c) Cu < Zn (d) Cu > Ni  
 (e) Zr = Hf (f) Ca > Sc  
 (g) Cr < Mo

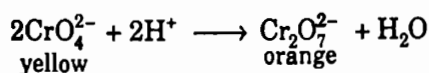
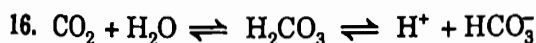
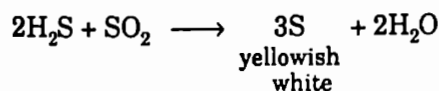
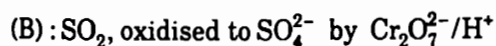
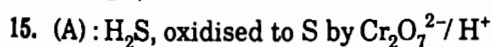
| B.  | Element (Z) | S     | $Z^* = Z - S$ |
|-----|-------------|-------|---------------|
| (a) | Sc(21)      | 18.0  | 3.0           |
| (b) | Ti(22)      | 18.85 | 3.15          |
| (c) | V(23)       | 19.70 | 3.30          |
| (d) | Cr(24)      | 20.55 | 3.45          |
| (e) | Mn(25)      | 21.40 | 3.60          |
| (f) | Fe(26)      | 22.25 | 3.75          |
| (g) | Co(27)      | 23.10 | 3.90          |
| (h) | Ni(28)      | 23.95 | 4.05          |
| (i) | Cu(29)      | 24.80 | 4.20          |
| (j) | Zn(30)      | 25.65 | 4.35          |



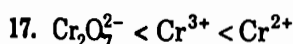
It is a redox reaction

—  $\text{NH}_4^+$  ion is oxidised to  $\text{N}_2$

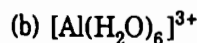
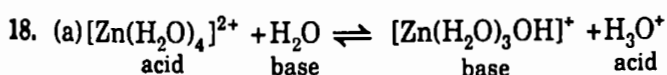
—  $\text{Cr}_2\text{O}_7^{2-}$  ion is reduced to  $\text{Cr}^{3+}$



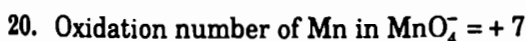
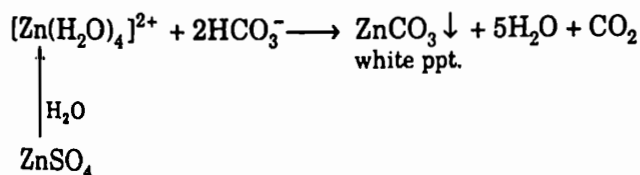
Aqueous  $\text{CO}_2$  is acidic and changes yellow  $\text{CrO}_4^{2-}$  into orange  $\text{Cr}_2\text{O}_7^{2-}$



Smaller the oxidation state of the element in the ion, greater the reducing nature.

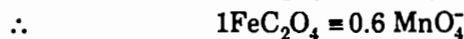
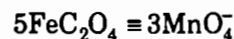
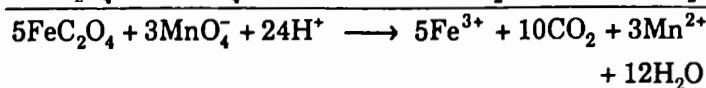
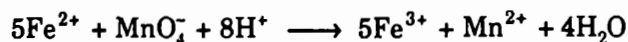
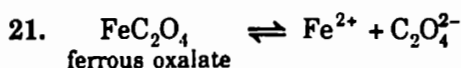


19.  $\text{ZnSO}_4$  solution is acidic due to hydrolysis. When  $\text{NaHCO}_3$  is added to it,  $\text{CO}_2$  is given off and  $\text{ZnCO}_3$  is also precipitated:



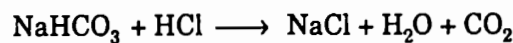
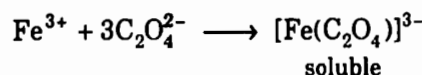
It is expected that (Mn in)  $\text{MnO}_4^-$  should have [Ar] configuration and should be colourless. But one electron is transferred to Mn from oxygen and thus Mn in  $\text{MnO}_4^-$  has one unpaired electron making it paramagnetic.

$$\text{Magnetic moment} = \sqrt{N(N+2)} = \sqrt{3} \text{ BM}$$

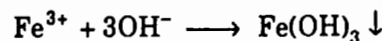


(Note Both  $\text{Fe}^{2+}$  and  $\text{C}_2\text{O}_4^{2-}$  are oxidised by  $\text{MnO}_4^-$ . Ask your teacher if one takes one mole of ferric oxalate)

22. Oxalic acid forms a dark-coloured complex with rust stains ( $\text{Fe}^{3+}$ ). This complex is water soluble. The rust stains can be removed by treating the fabric with oxalic acid and then washing with water.



24. (a) Excess of  $\text{KOH}$  separates  $\text{Fe}^{3+}$  as  $\text{Fe}(\text{OH})_3$



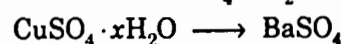
(b) Excess of  $\text{KOH}$  precipitates  $\text{Fe}^{3+}$  as  $\text{Fe}(\text{OH})_3$  while  $\text{Cr}^{3+}$  remains soluble  $\text{KCr}(\text{OH})_4$

(c) Excess of  $\text{NH}_3(\text{aq})$  precipitates  $\text{Fe}^{3+}$  as  $\text{Fe}(\text{OH})_3$  while  $\text{Cu}^{2+}$  remains soluble as  $[\text{Cu}(\text{NH}_3)_4]^{2+}$

White ppt. with  $\text{BaCl}_2 \Rightarrow \text{SO}_4^{2-}$

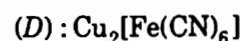
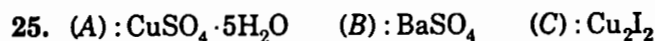
Chocolate coloured ppt with  $\text{K}_4[\text{Fe}(\text{CN})_6] \Rightarrow \text{Cu}^{2+}$

Thus, hydrated salt is :  $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$



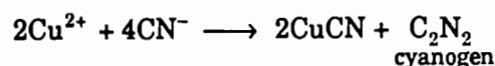
|             |      |
|-------------|------|
| 159.5 + 18x | 233  |
| 2.495       | 2.33 |

$$\therefore x = 5$$

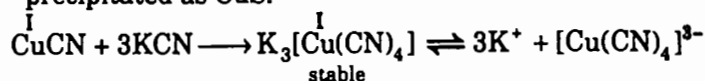


Reddish brown solution is due to formation of  $\text{KI}_3$  ( $\text{KI} + \text{I}_2 \rightleftharpoons \text{KI}_3$ ). On adding hypo,  $\text{I}_2$  is reduced to  $\text{I}^-$  and white ppt. of  $\text{Cu}_2\text{I}_2$  appears.

26. White precipitate is due to  $\text{CuCN}$



White precipitate of  $\text{CuCN}$  dissolves in excess of  $\text{KCN}$  due to formation of a soluble and stable complex  $[\text{Cu}(\text{CN})_4]^{3-}$  and even in the presence of  $\text{H}_2\text{S}$ ,  $\text{Cu}^{2+}$  is not precipitated as  $\text{CuS}$ .



$$\Delta G^\circ = \Delta G_f^\circ(\text{CO}) - \Delta G_f^\circ(\text{ZnO})$$

$$= -137.3 - (-318.2)$$

$$= 180.9 \text{ kJ mol}^{-1}$$



## Exercise 2

## Only One Option Correct

1. (d)
- $\text{Cu}^{2+}$
- is reduced to
- $\text{Cu}^+$
- by
- $\text{CN}^-$

Thus, (a) is true

 $\text{Cu}^+$  undergoes complexation with  $\text{CN}^-$  forming  $\text{K}_3[\text{Cu}(\text{CN})_4]$ . Thus, (b) and (c) are true

Thus, (d)

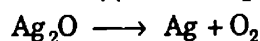
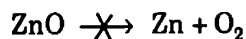
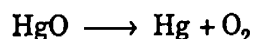
2. (c)

3. Larger anion stabilises to a greater extent.

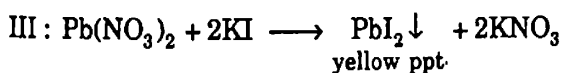
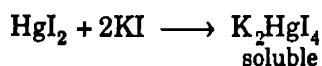
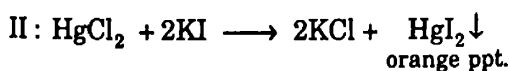
Thus, (a)

4. (c)

5. (b) Metals lying above H in electrochemical series are not obtained from their oxides by heating



6. I:
- $2\text{CuSO}_4 + 4\text{KI} \longrightarrow \text{Cu}_2\text{I}_2 + \text{I}_2 + \text{K}_2\text{SO}_4$
- 
- white ppt.



Thus, (b)

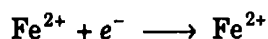
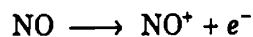
7. (b) 8. (d)

9. (c)
- $\text{NO} \longrightarrow \text{NO}^+ + e^-$

Oxidation state of Fe is +2 and  $\text{NO}^+$  is ligand

Thus, (c)

10. (a) Ring is formed by charge transfer

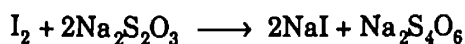


Thus, (a)

11. (c)

12. (b)
- $\text{Ni}^{2+} + \text{DMG} \longrightarrow [\text{Ni}(\text{DMG})_2]^{2+}$
- 
- cherry red ppt.

13. (a)
- $2\text{CuSO}_4 + 4\text{KI} \longrightarrow \text{K}_2\text{SO}_4 + \text{Cu}_2\text{I}_2 + \text{I}_2$



Thus, (a)

14. (c)

15. (d) Fe(III) gives red colours with KCNS

hence, (d) is incorrect.

16. (b) 17. (d) 18. (b) 19. (c) 20. (c)

21. (d)
- $\text{Cu}^+ : [\text{Ar}] 3d^{10}$

No unpaired electron, thus  $s = 0$ 

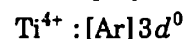
Thus, (d)

22. (a) 23. (c)

24. (c) II group (of cation-analysis) contains
- $\text{Pb}^{2+}$
- and
- $\text{Cu}^{2+}$
- and are precipitated as sulphides on passing
- $\text{H}_2\text{S}$
- in acidic medium.
- $\text{ZnS}$
- is precipitated in presence of
- $\text{NH}_4\text{OH}$
- and
- $\text{NH}_4\text{Cl}$
- .

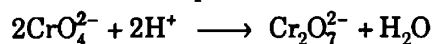
Thus, (c)

25. (b)
- $\text{Ti}(22) : [\text{Ar}] 4s^2 3d^2$
- |   |   |  |  |  |
|---|---|--|--|--|
| ↑ | ↑ |  |  |  |
|---|---|--|--|--|

 $\text{Ti}^{2+}$  has two unpaired electrons in  $3d$  and thus  $d-d^*$  transition is possible due to absorption of light in visible region.

26. (d)
- $2\text{Ag}^+ + \text{H}_2\text{S} \longrightarrow \text{Ag}_2\text{S}$
- (black)

27. (c)
- $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \longrightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$

 $\text{pH} > 7 (x > 7)$  $\text{pH} < 7 (y < 7)$ 

Thus, (c)

28. (a)
- $\text{MnO}_4^- \longrightarrow \text{MnO}_4^{2-} + e^-$

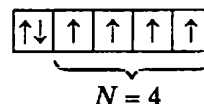
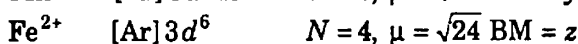
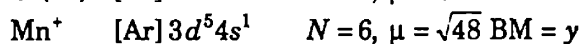
29. (b) In this case
- $\text{CrO}_2\text{Cl}_2$
- is formed

30. (c)
- $\text{MnO}_4^-$
- changes to
- $\text{MnO}_4^{2-}$
- or
- $\text{MnO}_2$
- in basic medium.

31. (a) 32. (c)

33. (a) Maximum unpaired electrons
- |   |   |   |   |   |
|---|---|---|---|---|
| ↑ | ↑ | ↑ | ↑ | ↑ |
|---|---|---|---|---|
- $d^5$

34. (c) Magnetic moment
- $\mu = \sqrt{N(N+2)} \text{ BM}$
- .

where,  $N$  = unpaired electronsThus,  $z < x = y$ 

Thus, (c)

35. (d)

36. (b) 24 carat gold is 100%

Thus, 22-carat gold is 91.67%

Thus, 3.5% higher

Thus, (b)

37. (c) 38. (a) 39. (c) 40. (b) 41. (c)

42. (c) 43. (a)



44. (b) generally salts are colourless due to  $d^{10}$ -configuration.

45. (c) 46. (a) 47. (d) 48. (a) 49. (b)

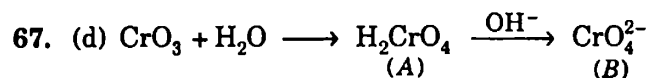
50. (c) 51. (c) 52. (a) 53. (c) 54. (c)

55. (a) 56. (a) 57. (c) 58. (a)

59. (d)  $\text{Mn}^{2+} (d^5)$   $\uparrow \uparrow \uparrow \uparrow \uparrow$

60. (d) 61. (b) 62. (b) 63. (d) 64. (c)

65. (a) 66. (c)



Thus, (d)

68. (a) 69. (c) 70. (c) 71. (d) 72. (b)

73. (a) 74. (a) 75. (c) 76. (d) 77. (a)

78. (d) 79. (b) 80. (b) 81. (c) 82. (a)

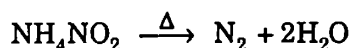
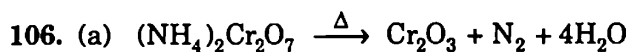
83. (b) 84. (b) 85. (b) 86. (b) 87. (c)

88. (d) 89. (b) 90. (d) 91. (a) 92. (d)

93. (a) 94. (c) 95. (b) 96. (d) 97. (d)

98. (b) 99. (b) 100. (c) 101. (b) 102. (a)

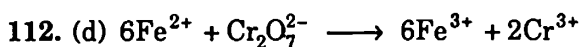
103. (c) 104. (b) 105. (a)



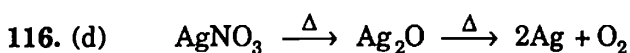
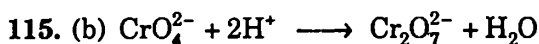
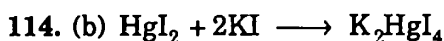
107. (b) 108. (d)

109. (b)  $[\text{Co}(\text{SCN})_4]^{2-}$ , cobalt is +2 with three unpaired electrons in  $3d$ . Thus,  $\mu = \sqrt{15}$  BM.

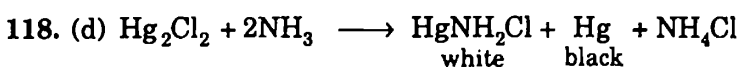
110. (b) 111. (b)



113. (b)

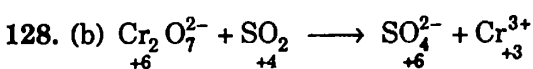


117. (c)



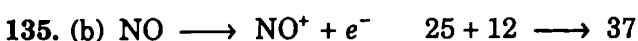
119. (d) 120. (d) 121. (a) 122. (a) 123. (b)

124. (d) 125. (a) 126. (c) 127. (c)



129. (d) 130. (a) 131. (b) 132. (b) 133. (c)

134. (d)



136. (a) 137. (b) 138. (b) 139. (d) 140. (c)

141. (a) 142. (b) 143. (c) 144. (a) 145. (c)

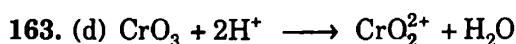
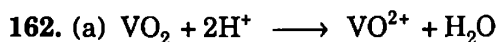
146. (b)  $\text{Cr}^{3+} : [\text{Ar}] 3d^5$  stable

147. (a) 148. (a) 149. (a) 150. (c)

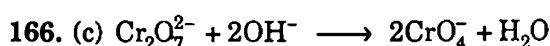
151. (a) 152. (b) 153. (c) 154. (c) 155. (a)

156. (c) 157. (d) 158. (b) 159. (c) 160. (b)

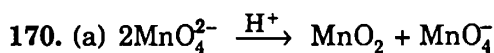
161. (a)



164. (b)



167. (d) 168. (c) 169. (c)

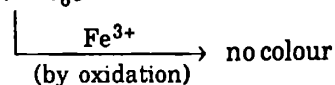
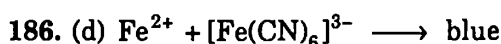
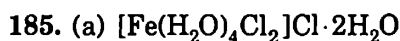


171. (a) 172. (d) 173. (b) 174. (a) 175. (c)

176. (b) ZnS is white.

177. (a) 178. (c) 179. (d) 180. (b) 181. (d)

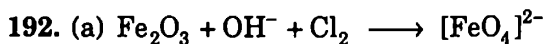
182. (c) 183. (a) 184. (a)



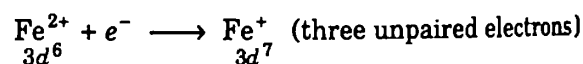
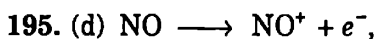
187. (a) 188. (d) 189. (b)

190. (c)  $\text{Fe}^{3+}$  forms soluble complex with oxalic acid.

191. (d)



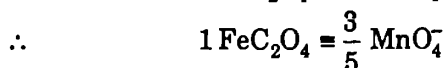
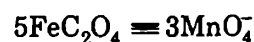
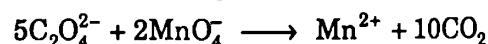
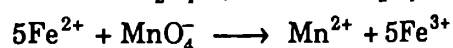
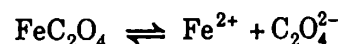
193. (b) 194. (c)



$$\text{Magnetic moment} = \sqrt{N(N+2)} = \sqrt{15} \text{ BM}$$

196. (c) 197. (b)

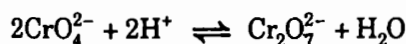
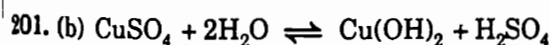
198. (a)  $\text{Fe}^{2+}$  as well  $\text{C}_2\text{O}_4^{2-}$  is oxidised by  $\text{MnO}_4^-$  in acidic medium



$$= 0.6 \text{ mol}$$

Thus, (a)

199. (b) 200. (c)



Thus, (b)

202. (c) 203. (d) 204. (b) 205. (c) 206. (d)

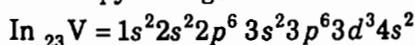
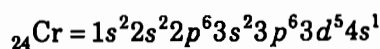
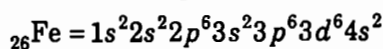
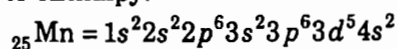
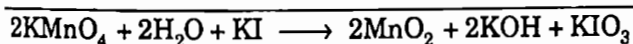
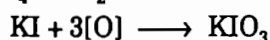
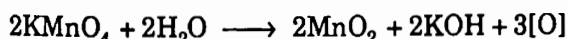
207. (b) 208. (b) 209. (b) 210. (c) 211. (c)

212. (d) 213. (d) 214. (a) 215. (a) 216. (d)

217. (c) 218. (c) 219. (b)

220. (a) Element (90-103) are in IIIB

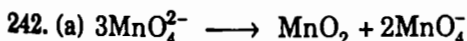
221. (d) 222. (d) 223. (a) 224. (c)

225. (d) Third electron which is removed in third ionisation potential enthalpy belongs to  $3d^3$  subshell in V.Third electron which is removed in third ionisation potential enthalpy belongs to  $3d^4$  subshell.Third electron which is removed in third ionisation potential enthalpy belongs to  $3d^6$  subshell.Third electron which is removed in third ionisation potential belongs to  $3d^5$  subshell.In all elements shell and subshells are same. Required amount of energy is based upon the stability of  $d$ -subshell. Hence, Mn shows highest third ionisation potential or enthalpy.226. (d) In alkaline solution,  $\text{KMnO}_4$  is reduced to  $\text{MnO}_2$  (black).Hence, 2 mol of  $\text{KMnO}_4$  are reduced to  $\text{MnO}_2$  by 1 mol of KI.

227. (a) 228. (b) 229. (d) 230. (d) 231. (b)

232. (b) 233. (b) 234. (b) 235. (d) 236. (b)

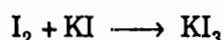
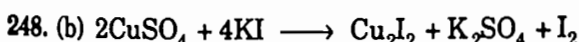
237. (c) 238. (a) 239. (d) 240. (d) 241. (c)



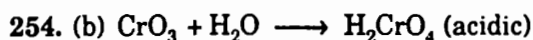
243. (c) 244. (a)

245. (b)  $\text{Cu}^+ : [\text{Ar}] 3d^{10}$  all electrons paired.

246. (b) 247. (c)

249. (b) 250. (a) 251. (c)  $[\text{Ar}] 4s^1 3d^5$ 

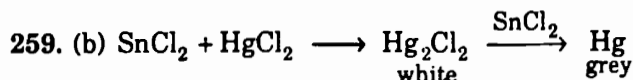
252. (a) 253. (d)



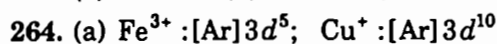
255. (c)

256. (c) Fe has 4 unpaired electrons

257. (c) 258. (c)



260. (b) 261. (d) 262. (c) 263. (b)



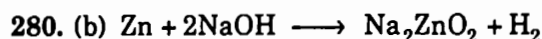
265. (a) 266. (c) 267. (d) 268. (d) 269. (c)

270. (a)

271. (c) Nascent H reduces NO to  $\text{NH}_3$  which changes to  $\text{NH}_4\text{NO}_3$ 

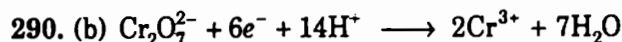
272. (c) 273. (a) 274. (d) 275. (b) 276. (b)

277. (c) 278. (c) 279. (b)



281. (b) 282. (d) 283. (a) 284. (c) 285. (d)

286. (d) 287. (d) 288. (b) 289. (c)



electron per Cr atom = 3

291. (a) 292. (a) 293. (a) 294. (b) 295. (a)

### One or More Than One Options Correct

1. (a,b,c) 2. (b,d) 3. (b) 4. (a) 5. (c)

6. (a,b) 7. (a,b,d) 8. (a,b,c) 9. (b) 10. (c)

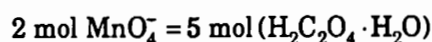
11. (a,b) 12. (a,b,c) 13. (c) 14. (a,d)

15. (a) 16. (a,b) 17. (a,b,d)

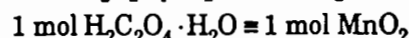
### Brain Twisters

1.  $\text{MnO}_4^-$  used =  $30.6 \times 0.1$  millimol

$$= 3.06 \times 10^{-3} \text{ mol}$$

thus,  $3.06 \times 10^{-3} \text{ mol } \text{MnO}_4^- = 7.65 \times 10^{-3} \text{ mol unreacted } (\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O})$ 

$$\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O} \text{ taken } \frac{1.651}{108} = 1.53 \times 10^{-2} \text{ mol}$$

Used  $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  by  $\text{MnO}_2 = 7.650 \times 10^{-3} \text{ mol}$ 

$$\therefore 7.64 \times 10^{-3} \text{ mol } \text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$$

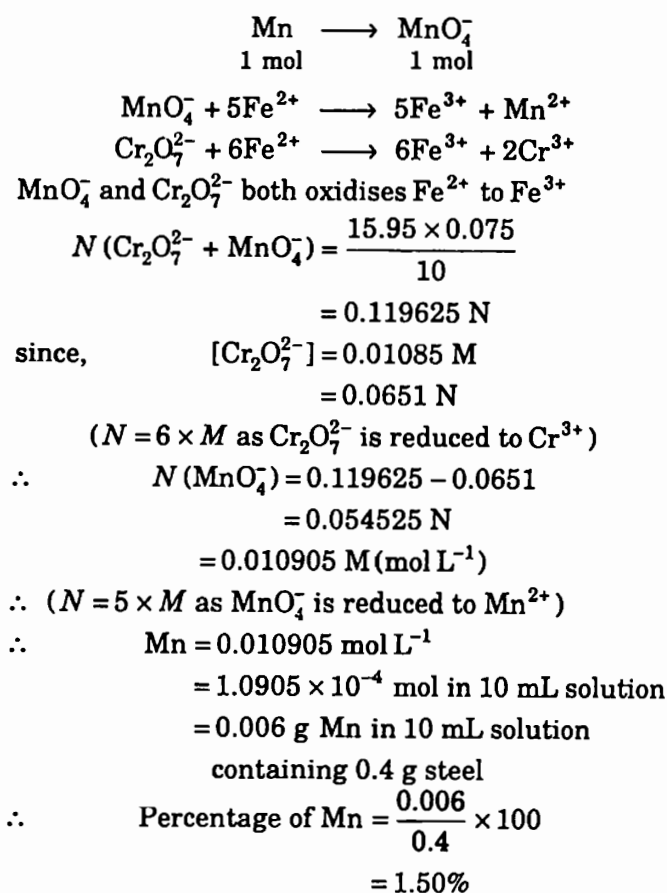
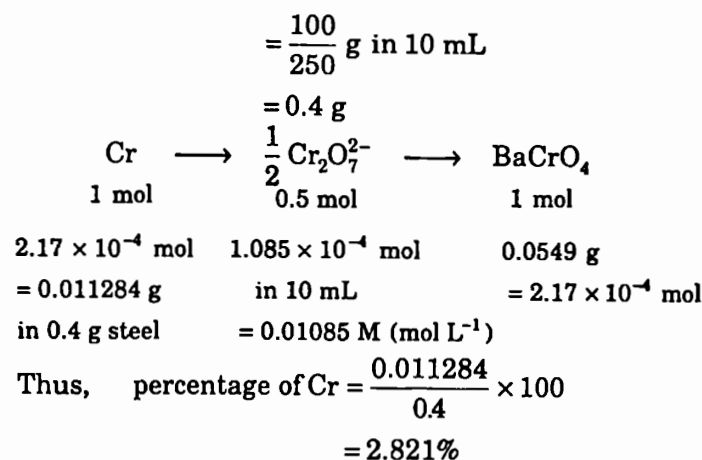
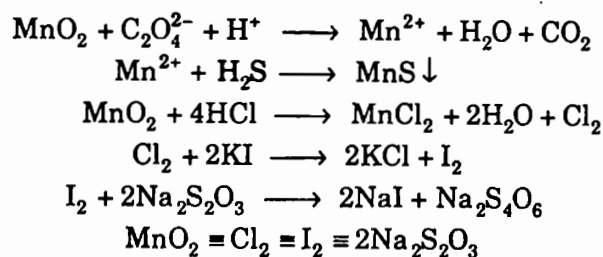
$$= 7.64 \times 10^{-3} \text{ mol } \text{MnO}_2$$

$$= 7.64 \times 10^{-3} \times 87 \text{ g pure } \text{MnO}_2$$

$$= 0.6644 \text{ g in } 0.81 \text{ g impure } \text{MnO}_2$$

$$\therefore \text{Percentage of pure } \text{MnO}_2 = \frac{0.6644}{0.81} \times 100 = 82.02\%$$

2. Cr is in the form of  $\text{Cr}_2\text{O}_7^{2-}$  and Mn is in the form  $\text{MnO}_4^-$ Steel content (as  $\text{MnO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$ ) = 10 g in 250 mL

3. (A):  $\text{MnO}_2$ 

(Mn = 55)

20 mL of  $\text{I}_2$  containing solution  $\equiv$  180 mL of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ 

$$\begin{aligned}
 N(\text{I}_2) &= \frac{180 \times 0.1}{20} \\
 &= 0.9 \text{ N}
 \end{aligned}$$

$$\text{Equivalent weight of } \text{MnO}_2 = \frac{\text{mol. wt.}}{2} = \frac{87}{2} = 43.5$$

Thus,  $\text{MnO}_2 = 0.9 \text{ N}$ 

$$\begin{aligned}
 \therefore \text{Conc in g/L} &= 0.9 \times 43.5 \text{ g/L} \\
 &= 39.15 \text{ g/L} \\
 \text{Thus, } \text{MnO}_2 \text{ in 200 mL} &= \frac{39.15}{5} = 7.83 \text{ g}
 \end{aligned}$$

| 4. Species           | Ionic/molar mass | %     | Mole ratio | Simplest ratio |
|----------------------|------------------|-------|------------|----------------|
| $\text{Co}^{3+}$     | 59.0             | 21.24 | 0.36       | 1              |
| $\text{Cl}^-$        | 35.5             | 12.81 | 0.36       | 1              |
| $\text{SO}_4^{2-}$   | 96               | 34.65 | 0.36       | 1              |
| $\text{NH}_3$        | 17               | 24.77 | 1.45       | 4              |
| $\text{H}_2\text{O}$ | 18               | 6.53  | 0.36       | 1              |

Thus, empirical formula is :  $[\text{Co}(\text{NH}_3)_4(\text{SO}_4)(\text{Cl})(\text{H}_2\text{O})]$ 

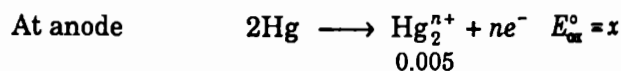
## 5. Coordination number of cobalt = 6

Since, one mole of the complex gives one mole of  $\text{AgCl}$  on reaction with  $\text{AgNO}_3$ , only one  $\text{Cl}$  is outside coordination sphere, and two  $\text{Cl}$  satisfy primary and secondary valency. Out of five water molecules, four are as ligand and remaining one water unit makes the complex hydrated. Thus complex is  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$

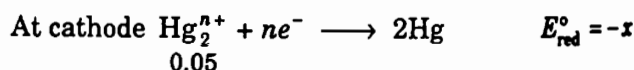
6. Let charge on the mercurous ion =  $n$ 

= number of electrons exchanged

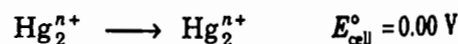
## Reactions

 $E^\circ$ 

0.005



0.05



0.05 M

0.005 M

$$K = \frac{0.005}{0.05} = \frac{1}{10}$$

$$\therefore E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0501}{n} \log \frac{1}{10}$$

$$0.0295 = 0 + \frac{0.0591}{n} \log 10$$

$$\therefore n = 2$$

## 7. Using equation

$$\Delta T_f \text{ (depression in freezing point)} = \frac{1000K_f w_1(i)}{m_1 w_2}$$

where,  $K_f$  = molar depression constant =  $1.86^\circ \text{ mol}^{-1} \text{ kg}$  $w_1$  = mass of solute = 0.875 g $w_2$  = mass of solvent = 25.0 g

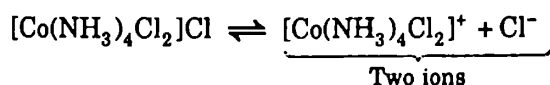
$$\Delta T_f = 0.56^\circ$$

 $i$  = van't Hoff factor = Number of ions from one mole complex (solute) $m_1$  = molar mass of solute

$$0.56^\circ = \frac{1000 \times 1.86 \times 0.875(i)}{233.5 \times 25}$$

$$i = 2$$

Thus, only one  $\text{Cl}^-$  is outside coordination sphere ( $\text{NH}_3$  is not ionisable).



## Passage Comprehension Questions

### Passage 1

1. (d) 2. (a) 3. (b)

### Passage 2

1. (c) 2. (b) 3. (a)

### Passage 3

1. (b) 2. (d) 3. (b) 4. (b) 5. (c) 6. (a)

### Passage 4

1. (d) 2. (c)

### Passage 5

1. (d) 2. (c) 3. (a) 4. (c)

### Passage 6

1. (c) 2. (a) 3. (d) 4. (b) 5. (d)

### Passage 7

1. (a) 2. (b)

### Passage 8

1. (c) 2. (b)

### Passage 9

1. (a) 2. (c)

### Passage 10

1. (b) 2. (a) 3. (a) 4. (c) 5. (d)

### Passage 11

1. (c) 2. (b) 3. (a)

### Passage 12

1. (a) 2. (b) 3. (c)

### Passage 13

1. (b) 2. (d) 3. (a)

## Assertion & Reason

1. (a) 2. (b) 3. (b) 4. (b) 5. (b) 6. (a)  
7. (e) 8. (b) 9. (d) 10. (d) 11. (c) 12. (b)  
13. (a)

## True & False

1. T 2. T 3. F 4. T 5. T 6. F  
7. F 8. T 9. T 10. T 11. F 12. F  
13. T 14. T 15. T 16. F 17. F 18. F  
19. T 20. F 21. T 22. T 23. T 24. F  
25. T 26. F 27. F 28. T 29. F 30. T  
31. F 32. T 33. T 34. F 35. T

## Fill in the Blanks

1.  $\text{FeCl}_3$  2. oxalic acid,  $\text{Fe}^{3+}$
3. diamagnetic, diamagnetic
4.  $\sqrt{15}$ , three 5.  $\text{Fe}^+$  and  $\text{NO}^+$  6. +2,  $\text{NO}^+$
7. magnetic moment 8. diamagnetic, square planar
9. 'wonder' 10. corrosion.
11. colourless (white),  $d-d^*$
12. charge transfer,  $\text{O}^{2-}$ , Mn (+VII)
13.  $\text{O}^-$ , Mn(VI), coloured.
14.  $\sqrt{24}$  BM, smaller ( $\text{Fe}^{2+}$  has  $3d^6 4s^0$ , Cr has  $3d^5 4s^1$  EC)
15. nonstoichiometric, metal
16. equal 17. lanthanide contraction
18. contact,  $\text{H}_2\text{SO}_4$  19.  $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ , acidic
20. Ferrochrome 21.  $\text{MnO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$
22.  $\text{CrO}(\text{O}_2)_2$  (a diperoxo compound), +6. 23. +5
24.  $(\text{NH}_3)_3\text{Cr}(\text{O}_2)_2$  (with two peroxide) 25.  $\text{CrO}_2^{2+}$
26.  $\text{Cr}_2\text{O}_3$ , reduction,  $\text{N}_2$ , oxidation.
27. acidic, alkali (say NaOH) 28. acidic, alkaline
29.  $\text{Mn}^{2+}$ ,  $\text{MnO}_2$  30.  $\frac{1}{5}$  th,  $\frac{1}{3}$  rd
31.  $\text{MnO}_2$ ,  $\text{MnO}_4^-$  disproportionation
32. Fe, haemoglobin
33.  $\text{MnO}_3^+$  34.  $\text{Mn}_2\text{O}_7$  35.  $\text{Na}_4[\text{Fe}(\text{OH})_6]$
36.  $[\text{Fe}(\text{CN})_6]^-$  37. mixed,  $\overset{\text{II}}{\text{Fe}}\text{O}\overset{\text{III}}{\text{Fe}}_2\text{O}_3$
38.  $\text{Fe}_2\text{O}_3$ , NaOH 39.  $\text{CuSO}_4$  40. KI, hypo

## Matrix-Match Type Questions

### I. Only One Correct

1. (A)–(2); (B)–(4); (C)–(3); (D)–(1);
2. (A)–(2); (B)–(1); (C)–(4); (D)–(3);
3. (A)–(3); (B)–(4); (C)–(1); (D)–(2);
4. (A)–(4); (B)–(5); (C)–(1); (D)–(2); (E)–(3)
5. (A)–(3); (B)–(1); (C)–(2); (D)–(5); (E)–(4)
6. (A)–(4); (B)–(3); (C)–(1); (D)–(2);
7. (A)–(2); (B)–(3); (C)–(4); (D)–(1);
8. (A)–(5); (B)–(4); (C)–(3); (D)–(2); (E)–(1)
9. (A)–(3); (B)–(1); (C)–(2); (D)–(5); (E)–(4)
10. (A)–(2-Q); (B)–(1-P); (C)–(3-R); (D)–(4-S);
11. (A)–(3); (B)–(1); (C)–(2); (D)–(4)

### II. One or More Correct

1. (A)–(1,3,4); (B)–(1,4); (C)–(2); (D)–(2,5)  
(E)–(1,4)
2. (A)–(2,6); (B)–(1,5,7); (C)–(2,3,6,7);  
(D)–(2,4,6,7) (E)–(2,6)

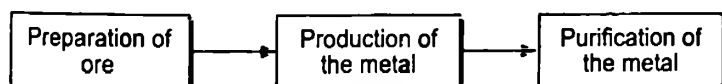


"Gold, silver, copper, tin and iron were probably the metals discovered by our ancestors"

# Metallurgical Extraction

**Metallurgy** is the science and technology of separating metals from their ores and of compounds alloys. An **alloy** is a solid solution either of two or more metals, or of a metal or metals with one or more non-metals.

Recovery of a metal from its ores involves three principal steps (three P's)



## Learning Framework of the Chapter

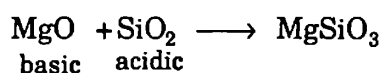
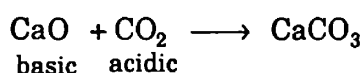
- The Occurrence and Isolation of the Elements
- Extraction of Copper
- Extraction of Magnesium
- Extraction of Lead
- Extraction of Tin
- Extraction of Silver
- Extraction of Aluminium
- Extraction of Iron
- Extraction of Zinc

## The Occurrence and Isolation of the Elements

- Most metals occur in nature as **minerals**; silicates and aluminates are the most abundant minerals (Table 17.1), but they are difficult to concentrate and reduce and therefore generally unimportant for commercial source of metals. Other minerals are oxides as haematite ( $\text{Fe}_2\text{O}_3$ ) and rutile ( $\text{TiO}_2$ ) and sulphides as cinnabar ( $\text{HgS}$ ) and galena ( $\text{PbS}$ ). Principal ores of some important metals have been summarised in Table 17.2.

## DEEP Focus

- The early transition metals on the left hand side of the *d*-block generally occur as oxides, and the more electronegative, late transition metals on the right hand side of the *d*-block occurs as sulphides. Less electronegative (more electropositive) metals can form ionic compounds by losing electrons to oxygen (and thus oxides are possible). More electronegative (less electropositive) metals tend to form covalent sulphide minerals with less electronegative sulphur.
- We might also expect to find oxide ores for the *s*-block metals and sulphide ores for the more electronegative *p*-block metals. In fact, sulphide ores are common for the *p*-block metals, except for Al and Sn.
- Oxides of the *s*-block metals are strongly basic hence, form carbonates and silicates with acidic oxides as  $\text{CO}_2$  and  $\text{SiO}_2$



- Only gold and platinum-group metals (Ru, Os, Rh, Ir, Pd and Pt) are sufficiently unreactive to occur as free metals (in natural state).
- The most abundant elements in the earth's crust (by weight) are shown in Table 17.1 and Fig. 17.1. This indicates :
  - oxygen is the most abundant element,
  - aluminium is the most abundant metal,
  - first five elements comprise almost 92% by weight, and
  - first ten elements make up over 99.5% of the earth's crust.

- Other very abundant elements are nitrogen (78% in the atmosphere) and hydrogen, which occurs as water in the ocean.

Table 17.1 The Most Abundant Elements

|     | Element    | % of Earth's crust |
|-----|------------|--------------------|
| 1.  | Oxygen     | 46.4               |
| 2.  | Silicon    | 28.2               |
| 3.  | Aluminium  | 8.32               |
| 4.  | Iron       | 5.63               |
| 5.  | Calcium    | 4.15               |
| 6.  | Sodium     | 2.36               |
| 7.  | Magnesium  | 2.14               |
| 8.  | Potassium  | 2.09               |
| 9.  | Titanium   | 0.57               |
| 10. | Hydrogen   | 0.14               |
| 11. | Phosphorus | 0.112              |
| 12. | Manganese  | 0.106              |

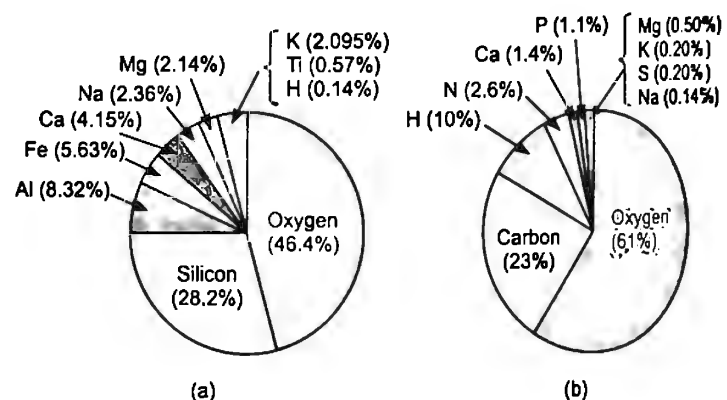


Fig. 17.1 Ten most abundant elements (a) In the earth's crust (b) In the human body

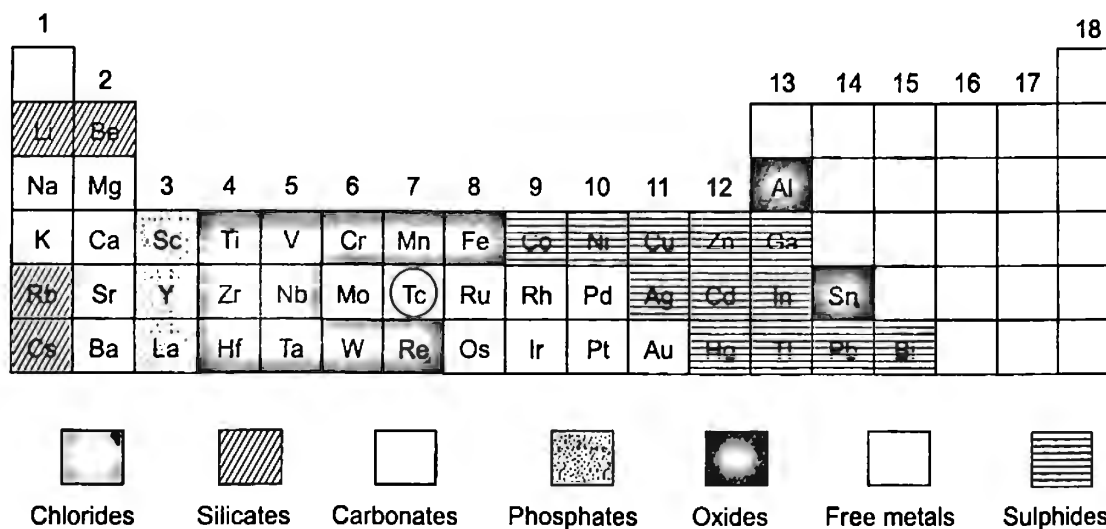


Fig. 17.2 Primary mineral sources of metals. The *s*-block metals occur as chlorides, silicates, and carbonates. The *d*- and *p*-block metals are found as oxides and sulphides, except for the group 3 metals, which occur as phosphates, and the platinum-group metals and gold, which occur in uncombined form. There is no mineral source of technitium (Tc in group 7), a radioactive element that is made in nuclear reactors.

Table 17.2 Principal Ores of Some Important Metals

| Metal     | Ore          | Formula                                            |
|-----------|--------------|----------------------------------------------------|
| Aluminium | Bauxite      | $\text{Al}_2\text{O}_3 \cdot x \text{H}_2\text{O}$ |
| Chromium  | Chromite     | $\text{FeCr}_2\text{O}_4$                          |
| Copper    | Chalcopyrite | $\text{CuFeS}_2$                                   |
| Iron      | Haematite    | $\text{Fe}_2\text{O}_3$                            |
| Lead      | Galena       | $\text{PbS}$                                       |
| Manganese | Pyrolusite   | $\text{MnO}_2$                                     |
| Mercury   | Cinnabar     | $\text{HgS}$                                       |
| Tin       | Cassiterite  | $\text{SnO}_2$                                     |
| Titanium  | Rutile       | $\text{TiO}_2$                                     |
|           | Ilmenite     | $\text{FeTiO}_3$                                   |
| Zinc      | Sphalerite   | $\text{ZnS}$                                       |

Table 17.2 and Fig. 17.2 summarise principal type of minerals as anion. Other minerals have been given in Appendix I

Table 17.3 Principal Types of Minerals Representing as Anions

| Type              |                                                                                                                                                                                                                                                                     |
|-------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Uncombined metals | Ag, Au, Bi, Cu, Pd, Pt<br>(Native ores)                                                                                                                                                                                                                             |
| Carbonates        | $\text{CaCO}_3$ (calcite, limestone), $\text{MgCO}_3$ (magnesite), $\text{CaCO}_3 \cdot \text{MgCO}_3$ (dolomite), $\text{PbCO}_3$ (cerussite), $\text{ZnCO}_3$ (smithsonite), $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$ (malachite), $\text{FeCO}_3$ (siderite) |
| Halides           | $\text{CaF}_2$ (fluorite), $\text{NaCl}$ (halite or rock salt), $\text{KCl}$ (sylvite), $\text{Na}_3\text{AlF}_6$ (cryolite), $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (carnallite), $\text{AgCl}$ (horn silver)                                  |

Table 17.4 Methods of Concentration of the Ore

| Method                                               | Ores specification                                                                                                                                                                                                                                                                                                                                                                                                                                       | Process                                                                                                                                                                                                                                                                                                                |
|------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1. Gravity separation (Tabling) by hydraulic washing | Based on the difference in the specific gravities of the ore and gangue. Cassiterite or tin-stone, chromite and pitchblende are concentrated                                                                                                                                                                                                                                                                                                             | Crushed ore is kept on top of a slope table, which is made to vibrate. A stream of water is passed in the direction perpendicular to the slope. The lighter particles are thrown up by vibration and are removed by water stream                                                                                       |
| 2. Magnetic separation                               | Based on the difference in magnetic properties of minerals. If the ore but not the gangue is attracted by a magnetic field, it can be concentrated to yield a sample which is rich in metal. Magnetite ( $\text{Fe}_3\text{O}_4$ ), haematite ( $\text{Fe}_2\text{O}_3$ ), wulframite ( $\text{FeWO}_4$ ), chromite ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ) and ilmenite ( $\text{FeO} \cdot \text{TiO}_2$ ) separated from non-magnetic impurities | The pulverised mineral is passed over a rubber belt which moves on a pulley in a magnetic field. The non-magnetic gangue particles fall off in a vertical position when the belt passes over a pulley, but the magnetic ore clings to the belt. When the belt is out of magnetic field, the ore separates. (Fig. 17.3) |

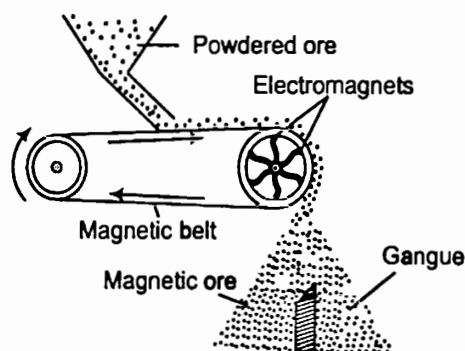


Fig. 17.3 Magnetic separation of ores

## Type

|            |                                                                                                                                                                                                                                                                                                                                                                          |
|------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Oxides     | $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (bauxite), $\text{Cu}_2\text{O}$ (cuprite), $\text{MnO}_2$ (pyrolusite), $\text{SnO}_2$ (cassiterite), $\text{Al}_2\text{O}_3$ (corundum), $\text{Fe}_2\text{O}_3$ (haematite), $\text{TiO}_2$ (rutile), $\text{ZnO}$ (zincite), $\text{Fe}_3\text{O}_4$ (magnetite)                                                   |
| Phosphates | $\text{Ca}_3(\text{PO}_4)_2$ (phosphate rock), $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (hydroxyapatite), $3\text{Pb}_3(\text{PO}_4)_2 \cdot \text{PbCl}_2$ (pyromorphite)                                                                                                                                                                                                  |
| Silicates  | $\text{NaAlSi}_3\text{O}_8$ (albite), $\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$ (talc), $\text{CaMg}_3\text{Si}_4\text{O}_{12}$ (asbestos), $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (felspar), $2\text{ZnO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ (hemimorphite), $\text{KAl}_3\text{H}_2\text{Si}_3\text{O}_{12}$ (mica) |
| Sulphides  | $\text{Ag}_2\text{S}$ (argentite), $\text{CdS}$ (greenockite), $\text{Cu}_2\text{S}$ (chalcocite), $\text{FeS}_2$ (pyrite), $\text{HgS}$ (cinnabar), $\text{PbS}$ (galena), $\text{ZnS}$ (sphalerite), $\text{CuFeS}_2$ (chalcopyrite), $\text{NiS}$ (nickel blende)                                                                                                     |
| Sulphates  | $\text{BaSO}_4$ (barite), $\text{CaSO}_4$ (anhydrite), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (epsomite), $\text{PbSO}_4$ (anglesite), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum)                                                                                                                                                                             |

## Benefication of Ores

Most of the ores available in nature contain large amount of impurities, i.e., gangue. The pretreatment of ores, based on physical properties and without bringing out any major chemical change in the ore, is known as **benefication or concentration of the ore or ore-dressing**.

Table (17.4) summarises the various methods adopted for the ore-dressing



| Method                            | Ores specification                                                                                                                                                                                                                                                         | Process                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
|-----------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 3. <b>Froth flotation process</b> | Used to concentrate sulphide ores, based on the difference in wettability of different minerals                                                                                                                                                                            | Refer Fig. 17.5. Sometimes depressants are used to prevent certain type of particles from forming the froth with the bubbles. NaCN is used as a depressants in the separation of CuS and PbS. NaCN acts a depressant for ZnS but does not prevent PbS from the formation of the froth, due to water soluble complex formation.<br>$\text{ZnS} + 4\text{NaCN} \longrightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + \text{Na}_2\text{S}$ Some additives increase the efficiency of this process. Cresols (froth stabiliser) increase the life time of froth.                                                                                                                 |
| 4. <b>Leaching</b>                | Useful in case the ore is soluble in a suitable solvent.<br>Pure $\text{Al}_2\text{O}_3$ is obtained from the bauxite ore in the Baeyer's process by leaching, also employed in concentration of silver and gold ores when leaching is done using NaCN in presence of air. | Leaching of bauxite<br>$\text{Al}_2\text{O}_3(\text{s}) + 2\text{OH}^-(\text{aq}) + 3\text{H}_2\text{O} \longrightarrow 2\text{Al}(\text{OH})_4^-$ $\xrightarrow[\text{CO}_2]{\text{dilution}} \text{Al}(\text{OH})_3 + \text{OH}^- \xrightarrow{\Delta} \text{Al}_2\text{O}_3$ $\text{Fe}_2\text{O}_3$ if present as impurity is not affected.<br>Leaching of silver and gold<br>$4\text{M} + 8\text{CN}^- + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow [\text{M}(\text{CN})_2]_{\text{soluble}}^-$ $(M = \text{Ag or Au})$ $\text{Ag}_2\text{S} + 4\text{CN}^- \longrightarrow 2[\text{Ag}(\text{CN})_2]^- + \text{S}^{2-}$                                         |
| 5. <b>Calcination</b>             | Used when concentrated ore is in the form of hydroxide or carbonate; volatile matter is burnt away. It is done in a reverberatory furnace.                                                                                                                                 | $2\text{Al}(\text{OH})_3 \xrightarrow{\Delta} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$ $\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$ It also drives out any organic matter that remains with the ore after concentration. It also removes moisture or water of crystallisation<br>$2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \longrightarrow 2\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$                                                                                                                                                                                                                                                       |
| 6. <b>Roasting</b>                | Sulphide ore is heated in a regular supply of air at a temperature below the melting point of the metal. It converts sulphide into oxide or sulphate; part of sulphide may also act as a reducing agent.                                                                   | $2\text{ZnS} + 3\text{O}_2 \xrightarrow{\Delta} 2\text{ZnO} + 2\text{SO}_2$ $2\text{Cu}_2\text{S} + 3\text{O}_2 \xrightarrow{\Delta} 2\text{Cu}_2\text{O} + 2\text{SO}_2$ $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \xrightarrow{\Delta} 6\text{Cu} + \text{SO}_2$ Process is carried out in a reverberatory furnace. The impurities which form volatile oxides are also driven off during roasting.<br>$\text{P}_4 + 5\text{O}_2 \longrightarrow \text{P}_4\text{O}_{10}$ $\text{As}_4 + 5\text{O}_2 \longrightarrow \text{As}_4\text{O}_{10}$ $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2 \uparrow$ $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2 \uparrow$ |

## Separation and Extraction of Elements

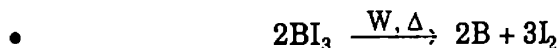
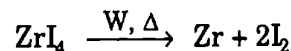
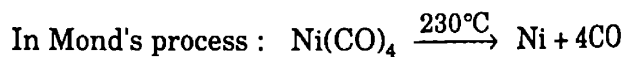
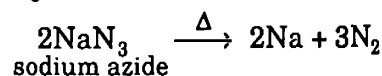
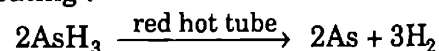
The different methods for separating and extracting elements may be divided into five classes :

**Mechanical Separation :** A surprisingly large number of elements occur in the free elemental state. They have remained in the native form because they are unreactive as Cu, Ag, Au and Pt.

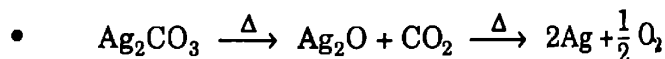
- Au is found in the native form, as grains in quartz, as nuggets and in the silt of river beds because of very high density ( $19.3 \text{ g cm}^{-3}$ ). Ag and Cu are sometimes found in the native form as nuggets. All the three metals lie below hydrogen and other reactive metals in electrochemical series and thus are easily displaced to the metallic form.
- Palladium and platinum are also found as native metals.
- Liquid droplets of Hg are found associated with cinnabar, HgS.

- Diamonds are found in the earth and are obtained by mechanical separation of large amount of earth and rock.

**Thermal Decomposition Method :** A few compounds will decompose into their constituent elements simply by heating :



- In van Arkel-de-Boer process :  $2\text{HgO} \xrightarrow{\Delta} 2\text{Hg} + \text{O}_2$



**DEEP Focus**

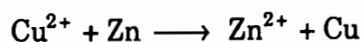
Oxides of the metals lying below Hg (and that of Hg) in electrochemical series decompose on heating giving metal.

A reaction is spontaneous if reducing agent is above oxidising agent in ECS.

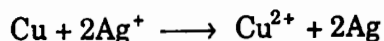
Zn and Mg can reduce  $\text{Fe}^{2+}$  to Fe (in prevention of rust) since both are above Fe in ECS.

**Displacement of Element by Another :** In principle any element may be displaced from solution by another element which is higher in electrochemical series (ECS).

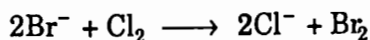
- Zn displaces Cu from  $\text{CuSO}_4$  solution since Zn is above Cu in ECS :



- Cu displaces Ag from  $\text{AgNO}_3$  solution due to the same fact:



- Sea water has  $\text{Br}^-$ .  $\text{Cl}_2$  can oxidise  $\text{Br}^-$  to  $\text{Br}_2$

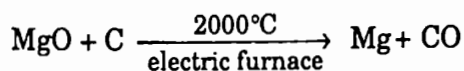
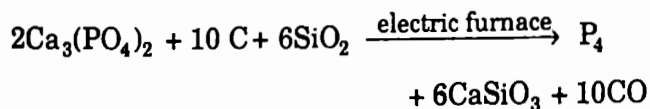
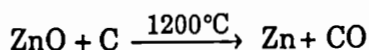
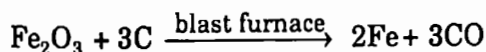


This method is quite applicable when displaced metal is costlier than the other metal which is oxidised. ECS is in order:

$\text{Li} > \text{K} > \text{Ca} > \text{Na} > \text{Mg} > \text{Al} > \text{Mn} > \text{Zn} > \text{Fe} > \text{Cu} > \text{Hg} > \text{Ag} > \text{Au}$

**High Temperature Chemical Reduction Methods :** Once an ore has been concentrated, it is reduced to the free metal, either by **chemical reduction** or by **electrolysis** as given in Tables 17.5 and 17.6. The method used depends on the activity of the metal as measured by its standard reduction potential. The most active metals have the most negative standard reduction potentials and are the most difficult to reduce; the least active metals have the most positive standard reduction potentials and are the easiest to reduce.

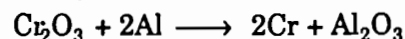
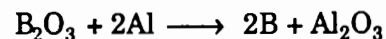
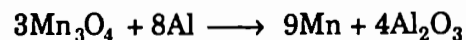
- **Reduction by carbon:**



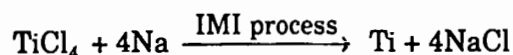
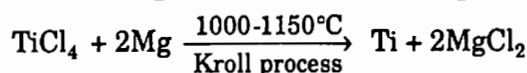
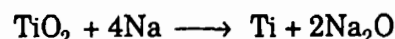
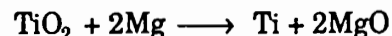
- **Reduction by another metal:**

If the temperature needed for carbon to reduce an oxide is too high for economic or practical purpose, the reduction may be affected by another highly electropositive metal such as aluminium, which liberates

a large amount of energy ( $1675 \text{ kJ mol}^{-1}$ ) on oxidation to  $\text{Al}_2\text{O}_3$ . This is the basis of the **thermite process** :

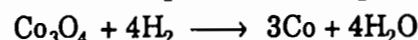
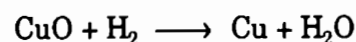


Magnesium is used in a similar way to reduce oxides in certain cases where the oxide is too stable to reduce, electropositive metals are used to reduce halides :



(IMI—Imperial Metal Industries)

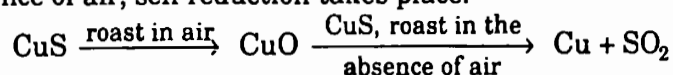
- **Reduction of oxides with  $\text{H}_2$ :**



This method is not widely used, because many metals react with  $\text{H}_2$  at elevated temperatures forming hydrides. Also there are chances of explosion of  $\text{H}_2$  with  $\text{O}_2$ .

- **Self reduction:**

Sulphides of Cu, Pb and Sb when roasted in air are converted partially into oxides. On further roasting in the absence of air, self reduction takes place:



It is carried out in a **Bessemer converter** or **Pierce-Smith converter**.

**Electrolytic Reduction**

To get metal of high purity, electrochemical refining is done making impure metal as anode.

- **In an aqueous solution**

It is used in cases when the electrolyte is soluble in water and products do not react with it. Copper, Zn, Ag and other metal are obtained by the electrolysis of aqueous solution of their salts ( $\text{ZnSO}_4$ ,  $\text{AgNO}_3$ ,  $\text{CuSO}_4$ ). Impure metal is oxidised at anode and is deposited at the cathode (of pure metal).

- **In fused melts:**

Na, K, Ca, Mg etc., react with  $\text{H}_2\text{O}$  hence, these metals are extracted by electrolysis of fused halides.

- Na and  $\text{Cl}_2$  are obtained by electrolysis of fused  $\text{NaCl}$ .
- Al is obtained by the electrolysis of fused mixture of  $\text{Al}_2\text{O}_3$  and  $\text{Na}_3[\text{AlF}_6]$  (cryolite).

• **In other solvents:**

Electrolysis can be carried out in solvents other than water.  $F_2$  reacts violently with  $H_2O$  hence, it is produced by electrolysis of  $KHF_2$  in  $HF$ .

Table 17.5 Reduction Methods for Producing Some Common Metals

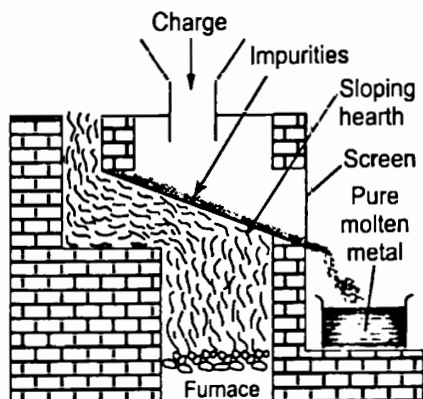
|              | Metal         | Reduction method                                                          |
|--------------|---------------|---------------------------------------------------------------------------|
| Least active | Au, Pt        | None; found in nature as the free metal                                   |
|              | Cu, Ag, Hg    | Roasting of the metal sulphide                                            |
|              | V, Cr, Mn, Fe | Reduction of the metal oxide with carbon, hydrogen or a more active metal |
|              | Al            | Electrolysis of molten $Al_2O_3$ in cryolite                              |
| Most active  | Li, Na, Mg    | Electrolysis of the molten metal chloride                                 |

Table 17.6 Some Specific Reduction Processes

| Metal     | Compound (ore)                         | Reduction process                                                                                                                                                                | Comments                                                                               |
|-----------|----------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|
| Mercury   | HgS (cinnabar)                         | Roast reduction; heating of ore in air<br>$HgS + O_2 \xrightarrow{\Delta} Hg + SO_2$                                                                                             |                                                                                        |
| Copper    | Sulphides such as $Cu_2S$ (chalcocite) | Blowing of oxygen through purified molten $Cu_2S$<br>$Cu_2S + O_2 \xrightarrow{\Delta} 2Cu + SO_2$                                                                               | Preliminary ore concentration and purification steps required to remove FeS impurities |
| Zinc      | ZnS (sphalerite)                       | Conversion to oxide and reduction with carbon<br>$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$ $ZnO + C \xrightarrow{\Delta} Zn + CO$                                          | Process also used for the production of lead from galena PbS                           |
| Iron      | $Fe_2O_3$ (haematite)                  | Reduction with carbon monoxide<br>$2C (\text{coke}) + O_2 \xrightarrow{\Delta} 2CO$ $Fe_2O_3 + 3CO \xrightarrow{\Delta} 2Fe + 3CO_2$                                             |                                                                                        |
| Titanium  | $TiO_2$ (rutile)                       | Conversion of oxide to halide salt and reduction with an active metal<br>$TiO_2 + 2Cl_2 + 2C \xrightarrow{\Delta} TiCl_4 + 2CO$ $TiCl_4 + 2Mg \xrightarrow{\Delta} Ti + 2MgCl_2$ | Also used for the reduction of $UF_4$ obtained from $UO_2$ , pitchblende               |
| Tungsten  | $FeWO_4$ (wolframite)                  | Reduction with hydrogen<br>$WO_3 + 3H_2 \xrightarrow{\Delta} W + 3H_2O$                                                                                                          | Used also for molybdenum                                                               |
| Aluminium | $Al_2O_3 \cdot nH_2O$ (bauxite)        | Electrolytic reduction (electrolysis) in molten cryolite. $Na_3[AlF_6]$ at $1000^\circ C$ .<br>$2Al_2O_3 \xrightarrow{\Delta} 4Al + 3O_2$                                        |                                                                                        |
| Sodium    | NaCl (sea water)                       | Electrolysis of molten chlorides<br>$2NaCl \xrightarrow{\Delta} 2Na + Cl_2$                                                                                                      | Also for calcium, magnesium, and other active metals in groups IA(1) and IIA(2)        |

Table 17.7 Refining of Crude Metals

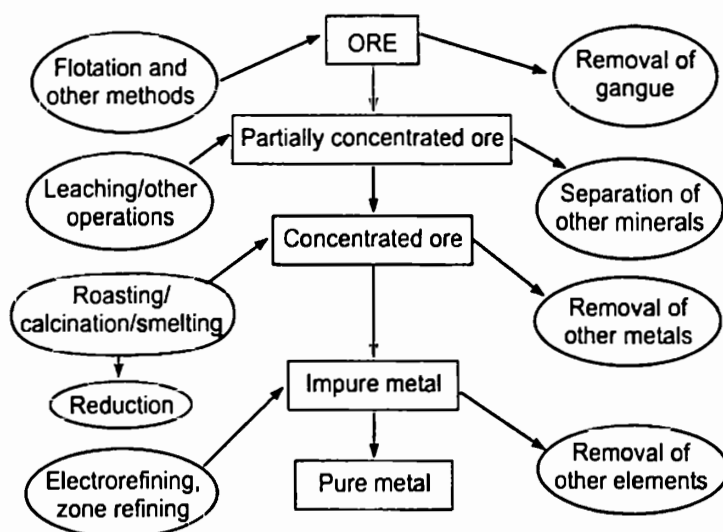
| Methods         | Metals purified                                                                                                                                                                                                                                                                                                                                                                                           |
|-----------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1. Distillation | Zinc, mercury and cadmium. This method is used in cases where metal has lower boiling point than impurities. Impure metal is heated to the boiling point in a closed retort when vapours formed are condensed to the pure metal. Non-volatile impurities are left unreacted.                                                                                                                              |
| 2. Electrolysis | Copper, gold, silver, lead, zinc, aluminium<br>Impure metal is made anode and the pure metal is cathode. The net result is the transfer of pure metal from anode to cathode.<br>At anode :<br>$\text{Cu (impure)} \longrightarrow \text{Cu}^{2+} + 2\text{e}^{-}$ At cathode :<br>$\text{Cu}^{2+} + 2\text{e}^{-} \longrightarrow \text{Cu (pure)}$ $\text{Cu (impure)} \longrightarrow \text{Cu (pure)}$ |
| 3. Liquation    | A low melting metal like tin can be made to flow on a sloping surface and thus separated from higher melting impurities.                                                                                                                                                                                                                                                                                  |



## 4. Zone refining

Metal of high purity are obtained. Silicon, germanium, boron, gallium, indium are purified. (which are used in semiconductors). It is based on the fact that impurities are more soluble in the melt than in the pure metal. Impure metal (in the form of rod) is moved through a circular heater. When melting point is reached, pure metal melts and impurities are concentrated in a particular zone and pure metal in the other zone and crystallises out. Process is repeated several times.

| Methods            | Metals purified                                                                                                                                                                                                                                                                                                                                                                                              |
|--------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 5. Vapour refining | phase In Mond process for the refining of nickel<br>$\text{Ni (impure)} + 4\text{CO} \xrightarrow{80^{\circ}\text{C}} \text{Ni(CO)}_4$ $\xrightarrow{200^{\circ}\text{C}} \text{Ni (pure)} + 4\text{CO} \uparrow$ In van Arkel method for zirconium<br>$\text{Zr (impure)} + 2\text{I}_2 \xrightarrow{600^{\circ}\text{C}} \text{ZrI}_4$ $\xrightarrow{1800^{\circ}\text{C}} \text{Zr (pure)} + 2\text{I}_2$ |



## Factors Influencing the Choice of Extraction Process

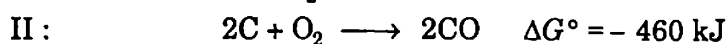
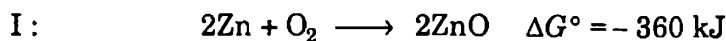
The type of process used commercially for any particular element depends on a number of factors :

- Is the element unreactive enough to exist in the free state?
- Are any of the compounds unstable to heat?
- Does the element exist as an ionic compound, and is the element stable in  $\text{H}_2\text{O}$ ?
- Is there a cheap element above it in the ECS which can be sacrificed to displace it from solution?
- Does the element occur as sulphide ores which can be roasted, or oxide ores which can be reduced by carbon (which can be the cheapest) or by Al, Mg and Na (which can be still costlier)?
- If all other methods fail, electrolysis is preferred (in aqueous solution which is the best to get metal of highest purity or in fused state which is again costlier).

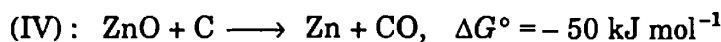
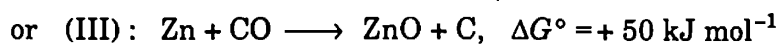
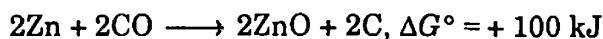
## Thermodynamics of Extractive Metallurgy

It is interesting to think of the reduction of  $\text{ZnO}$  with C as involving a competition between Zn and C for O atoms.

We consider following values at 1100°C for the oxidation of Zn and C :



(I)–(II) gives



For reaction III, in which Zn reduces CO,  $\Delta G^\circ$  is positive indicating that this reduction is not spontaneous (in forward direction), but for the reaction IV with negative value of  $\Delta G^\circ$ , in which C reduces ZnO is spontaneous. (in forward direction).

Why must we carry out the reduction of ZnO with C at 1100°C? From an energy stand point it would certainly be more economical to carry it out at a lower temperature. The graphical representation of Fig 17.4 (Ellingham diagram) is useful tool to help answer such questions. The lines ( $2\text{C} + \text{O}_2 \longrightarrow 2\text{CO}$ ) and ( $2\text{Zn} + \text{O}_2 \longrightarrow 2\text{ZnO}$ ) cross at about 950°C. At about this temperature Zn and C have equal affinities for O atoms:  $\Delta G^\circ$  for reaction (IV) is zero. Above this temperature  $\Delta G^\circ$  is negative, and below this temperature  $\Delta G^\circ$  is positive. To make reaction (IV) go essentially to completion we need a temperature somewhat in excess of 950°C.

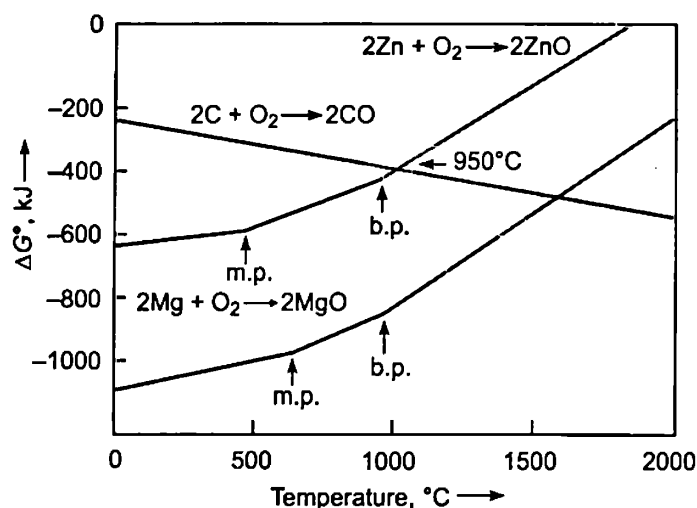


Fig. 17.4 The points noted by arrows are the melting and boiling points of the metals zinc and magnesium.  $\Delta G^\circ$  as a function of temperature for some reactions of extractive metallurgy.

## Extraction of Copper

### Occurrence

- Cuprite  $\text{Cu}_2\text{O}$
- Malachite  $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$
- Azurite  $2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$
- Copper pyrites or Chalcopyrites  $\text{CuFeS}_2$

Main source is copper pyrites. Some copper is also found in native state.

### Pyrometallurgical Method (Dry Method)

Sulphide ore is converted into copper in following steps :

**Step I : Concentration by Froth-Flotation process (Fig. 17.5)**

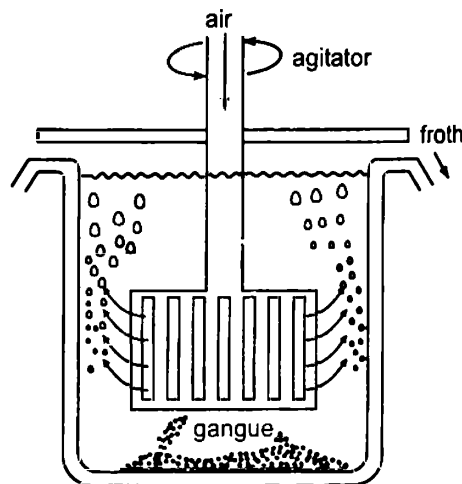
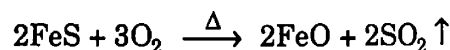


Fig. 17.5 Concentration of an ore by flotation

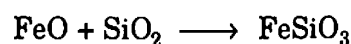
Powdered ore is suspended in water in a large vat, together with suitable additives, and the mixture is agitated with air. Particles of ore become attached to air bubbles, rise to the top of the vat, and are collected in the overflow froth. Particles of the undesired waste rock (gangue) fall to the bottom.

The success of this method depends on the use of proper additives—a material that will produce a stable foam (frother) and a substance (collector) that coats the particles of ore but does not “wet” the particles to be rejected. Pine oil is widely used as a frother and sodium ethyl xanthate ( $\text{C}_2\text{H}_5\text{OCS}_2\text{Na}$ ) as a collector.

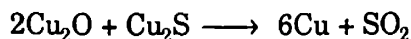
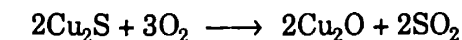
**Step II : Roasting** is done in multiple hearth furnace. Volatile impurities are removed as thin oxide ( $\text{As}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ). It also converts iron sulphide to iron oxide. The copper remains as the sulphide if the temperature is kept below 800°C.



**Step III : Smelting** of the roasted ore is done in a furnace at 1400°C. In this furnace charge melts and separates into two layers. The bottom layer is **copper-matte**, consisting chiefly of the molten sulphides of copper and iron. The top layer is a silicate slag formed by the reaction of oxides of Fe, Ca, and Al with  $\text{SiO}_2$  (which either is present in the ore or is added) and is removed.



**Step IV : Bessemerisation (or Converting)** occurs in another furnace where air is blown through the molten copper matte. First, the remaining iron sulphide is converted to oxide (as in step II) followed by slag formation (as in step III). The slag is poured off and air is again blown through the furnace. Now the following reactions occur, yielding a product that is about 98 to 99% Cu.



The product of this step is called **Blister copper** because of frozen bubbles of  $\text{SO}_2$ . It can be used where high purity is not required.

**Step V : Electrorefining :**

|             |                                                      |
|-------------|------------------------------------------------------|
| Anode       | : impure copper                                      |
| Cathode     | : pure copper                                        |
| Electrolyte | : 3.5% $\text{CuSO}_4$ + 15% $\text{H}_2\text{SO}_4$ |
| Voltage     | : 0.3 to 0.5 V                                       |
| Temperature | : $50.55^\circ\text{C}$                              |

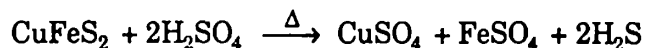
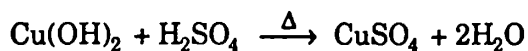
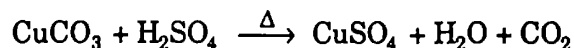
Cu from impure copper anode goes into solution and is deposited at the cathode :



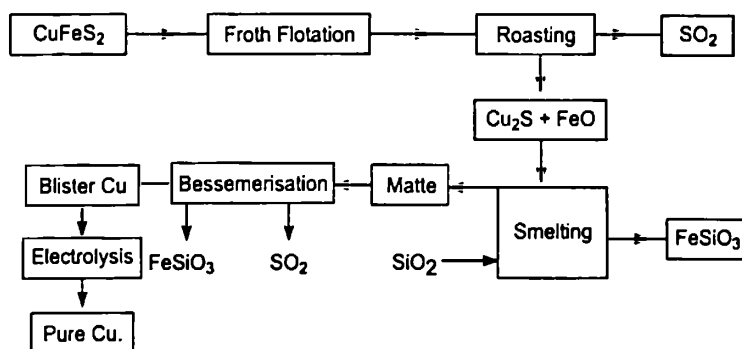
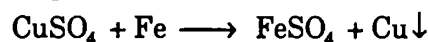
Anode-mud (anode-sludge) contains Au, Pt, Ag and other precious metals (noble metals).

## Hydrometallurgical Process (Wet Process)

**Step I : Leaching with  $\text{H}_2\text{SO}_4$**  converts salts into sulphates:



**Step II : Electrochemical Displacement :** Fe is above Cu in ECS, hence if Fe scrap is added to  $\text{CuSO}_4$  solution, Cu is displaced :



## Target Practice 1

- NaCl solution is neutral. If it undergoes electrolysis, pH increases/decreases/remains constant .....
- When Cu turnings are added to  $\text{AgNO}_3$  solution, it turns blue. It is due to formation of .....
- We have  $\text{CuSO}_4$  solutions (blue) in two beakers A and B. In beaker A we add Ag pieces and in B we add Zn pieces. What will happen?  
In A .....  
In B .....
- Name the process (unbalanced reactions)  
(a)  $2\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow \text{Cu}_2\text{O} + \text{SO}_2$   
 $\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow \text{Cu} + \text{SO}_2$  .....
- (b)  $\text{Ni} + 4\text{CO} \xrightarrow{80^\circ\text{C}} \text{Ni}(\text{CO})_4 \xrightarrow{200^\circ\text{C}} \text{Ni} + 4\text{CO} \uparrow$  .....
- (c)  $\text{Zn} + 2\text{I}_2 \xrightarrow{600^\circ\text{C}} \text{ZrI}_4 \xrightarrow{1800^\circ\text{C}} \text{Zn} + 2\text{I}_2$
- Write three minerals (in each case) which occur as  
(a) Sulphide .....  
(b) Oxide .....  
(c) Oxosalts .....
- You are living very near to sea-coast. What types of minerals can be present in direct supply of tap water?  
(i) ..... (ii) .....  
(iii) ..... (iv) .....
- What method can be used for beneficiation of the following?  
(i) Haematite .....  
(ii) Cassiterite .....
- (iii) Chromite .....
- (iv) Copper pyrites .....
- A mineral is rich in ZnS and PbS. Give scheme to concentrate it by froth flotation process.  
.....  
.....
- What are the main steps of pyrometallurgy?  
.....  
.....
- Explain the term hydrometallurgy with example.  
.....  
.....
- What are the criteria of selection of a good reducing agent for extraction of metals?  
.....  
.....
- Why is carbon reduction not used to obtain certain metals from their ores?
- From the Ellingham diagram (Fig. 17.4) compute the temperature of reduction of  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  by carbon  
.....  
.....
- Define the terms  
(a) Copper matte .....  
(b) Blister copper .....  
(c) Anode-mud .....

- 15. Minerals are rich in the following as given**

**Mineral I:** Rich in AgCl, CuS, FeS

**Mineral II : Rich in ZnS, CuS, FeS**

**Mineral III : Rich in  $\text{Ag}_2\text{S}$ ,  $\text{ZnS}$ ,  $\text{FeS}$**

If concentration of the above minerals are done separately without knowing the presence of their contents, metals obtained in the native state from

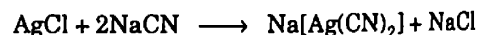
- (I) .....  
 (II) .....  
 (III) .....

- 16. Chemical reactions of the hydrometallurgical extraction of copper are**

## Answers

- Increases (NaCl in neutral; due to electrolysis NaOH is formed which being basic has  $\text{pH} > 7$ ).
- $\text{Cu}^{2+}(\text{aq})$
- In A : no reaction (Ag is not oxidised)  
In B :  $\text{Cu}^{2+}$  is reduced to Cu (which is displaced) by Zn which is oxidised. Solution becomes colourless or fades.
- (a) Bessemerisation (b) Mond's process (c) van Arkel
- (a) **Sulphide**  $\text{Ag}_2\text{S}$  (argentite),  $\text{HgS}$  (cinnabar),  $\text{PbS}$  (galena)  
(b) **Oxide**  $\text{Cu}_2\text{O}$  (cuprite),  $\text{Fe}_3\text{O}_4$  (magnetite),  $\text{TiO}_2$  (rutile)  
(c) **Oxo salts**  $\text{BaSO}_4$  (barite),  $\text{Ca}_3(\text{PO}_4)_2$  (phosphate rock).  
 $\text{CaCO}_3$  (calcite)
- (i) NaCl (ii) NaBr (iii) NaI (iv)  $\text{MgCl}_2$
- (i) Magnetic separation  
(ii) Gravity method  
(iii) Magnetic separation or gravity method  
(iv) Froth flotation process
- $\text{NaCN}$  is added benefication by froth flotation process (FFP).  $\text{ZnS}$  is converted to soluble complex  $\text{Na}_2[\text{Zn}(\text{CN})_4]$  and  $\text{PbS}$  goes into froth by FFP.
- In pyrometallurgy, the concentration ore is heated to a high temperature and reduction is done with a suitable reducing agent. Steps involved are  
(a) Calcination, (b) Roasting, (c) Smelting
- Hydrometallurgy is generally used in the case of low grade ores, which cannot be concentrated economically. The

powdered ore is first treated with an aqueous solution of a suitable chemical whereby the metal is obtained in the form of its soluble salts leaving behind gangue particles. (leaching)



11. A good reducing agent for extraction of metals should possess the following properties
  - (i) It should be cheaper than the metal being produced.
  - (ii) It should be able to reduce the metal compounds to free metal in a pure form at a suitable temperature.
  - (iii) It should not combine with the metal being produced.
12. Carbon reduction is not used to obtain certain metals from their ores because it can combine with them to produce metal carbides.
13.  $\text{MgO}$  : 1935 K  
 $\text{CaO}$  : 2445 K  
 $\text{TiO}_2$  : 1865 K  
 $\text{Al}_2\text{O}_3$  : 2570 K
14. Refer text
15. I : Ag      II : Cu      III : Ag
16. 
$$\text{CuO} + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{H}_2\text{O}$$
$$\text{CuCO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{H}_2\text{O} + \text{CO}_2$$
$$\text{Cu}_2\text{S} + 2\text{H}_2\text{SO}_4 + 2\text{O}_2 \longrightarrow 2\text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$$

## Practice Exercise 1

1. Look at the location of elements A, B, C and D in the following periodic table :

Predict whether these elements are likely to be found in nature as carbonates, oxides, sulphides or in uncombined state.

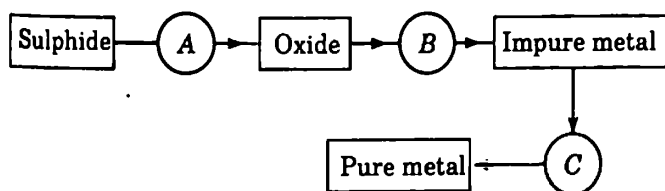
2. List three metals that are found in nature as oxide ores.
3. Explain, why early transition metals occur in nature as oxides but the late transition metals occur as sulphides.

4. Imagine a planet with an atmosphere that contains  $O_2$  and  $SO_2$  but no  $CO_2$ . Give the chemical composition of the minerals you would expect to find for the alkaline earth metals on such a planet.
5. Na metal can't be obtained by electrolysis of aqueous NaCl solution. Explain.
6. (A)  $Al_2O_3$  can't be reduced by carbon to get Al metal. Explain  
(B) NaCN is sometimes added in the froth flotation process as a depressant when ZnS and PbS minerals are expected because
  - (a)  $Pb(CN)_2$  is precipitated while no effect on ZnS
  - (b) ZnS forms soluble complex  $Na_2[Zn(CN)_4]$  while PbS forms froth
  - (c) PbS forms soluble complex  $Na_2[Pb(CN)_4]$  while ZnS forms froth
  - (d) NaCN is never added in froth flotation process
7. Cu can reduce  $Ag^+$  to metallic Ag but Ag can't reduce  $Cu^{2+}$  to metallic Cu. Explain.

8. Among the methods for extracting metals from their ores are (i) roasting a metal sulphide, (ii) chemical reduction of a metal oxide, and (iii) electrolysis. The preferred method depends on  $E^\circ$  value for the reduction half-reaction:



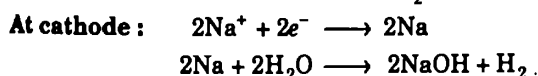
- (a) Which method is preferred for the metals with the most negative  $E^\circ$  values?  
 (b) Which method is preferred for the metals with the most positive  $E^\circ$  values?
9. The roasting of an ore of a metal usually results in conversion of the metal to the oxide. Why does the roasting of cinnabar,  $HgS$ , produce metallic mercury rather than an oxide of mercury?
10. A metal is in combined state as sulphide. Identify the steps (A), (B), (C)



11. Write chemical equations for metallurgical processes to represent :  
 (a) roasting of galena ( $PbS$ ),  
 (b) reduction of  $Cu_2O$  using charcoal as a reducing agent,  
 (c) deposition of pure silver from an aqueous solution of  $Ag^+$ ,
12. Write chemical equations to represent the most probable outcome in each of the following. If no reaction is likely to occur, state so:  
 (a)  $CdCO_3 \xrightarrow{\Delta}$  (b)  $MgO \xrightarrow{\Delta}$   
 (c)  $SnO_2 + CO \xrightarrow{\Delta}$  (d)  $CdSO_4(aq) \xrightarrow{\text{electrolysis}}$   
 (e)  $HgO \xrightarrow{\Delta}$  (f)  $MgO + Zn \xrightarrow{\Delta}$
13. Using data in Fig. 17.4, predict whether the reduction of  $MgO$  with  $C$  is spontaneous or not at  $1500^\circ C$ ?
14. Name two metals and two non-metals obtained by electrolysis.
15. The following reactions take place during the extraction of copper from copper ore:  
 (a)  $2Cu_2S(l) + 3O_2(g) \longrightarrow 2Cu_2O(l) + 2SO_2(g)$   
 (b)  $2Cu_2O(l) + Cu_2S(l) \longrightarrow 6Cu(l) + SO_2(g)$   
 Identify the oxidising and reducing agents.

## Answers

1. A : Oxide B : Sulphide C : Carbonate D : Free metal  
 2. Fe as  $Fe_3O_4$ , Ti as  $TiO_2$ , Sn as  $SnO_2$  3. Refer text  
 4.  $MSO_4$ ,  $MSO_3$   
 5. When aqueous  $NaCl$  solution is electrolysed,  $Cl_2$  is formed at the anode and  $Na$  at the cathode. But  $Na$  is very reactive with  $H_2O$  forming  $NaOH$  and  $H_2$ . Thus,  $Na$  can't be prepared by electrolysis of  $aq$   $NaCl$

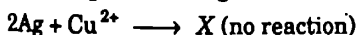


6. A.  $Al$  has greater affinity for  $O_2$  than carbon has, hence  $C$  can't be used to reduce  $Al_2O_3$  to  $Al$ . Thermodynamically for this reaction :



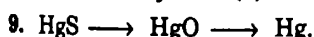
$\Delta G^\circ_f$  is positive hence, reaction is non-spontaneous.

B. (b)



In ECS,  $Cu$  is above  $Ag$  hence  $Cu$  can reduce  $Ag^+$  to metallic  $Ag$ .

8. (a) Electrolysis (b) Roasting a metal sulphide



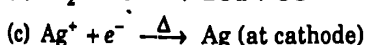
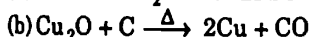
Since,  $Hg$  lies much below  $H$  in electrochemical series hence,  $HgO$  is further reduced to  $Hg$ .

10. (A) : roasting

(B) : reduction by carbon or more electropositive metal.

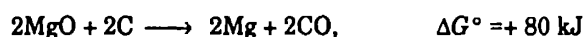
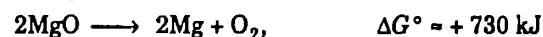
(C) : electrolysis

11. (a)  $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$



12. (a)  $CdCO_3 \xrightarrow{\Delta} CdO + CO_2$   
 (b) No reaction.  
 (c)  $SnO_2 + 2CO \xrightarrow{\Delta} Sn + 2CO_2$   
 (d)  $CdSO_4(aq) \xrightarrow{\text{current}} \underset{\text{at anode}}{H_2SO_4 + O_2} + \underset{\text{at cathode}}{Cd}$   
 (e)  $2HgO \xrightarrow{\Delta} 2Hg + O_2$   
 (f) no reaction

13. From Fig. 17.4 at  $1500^\circ C$



Or  $MgO + C \longrightarrow Mg + CO, \quad \Delta G^\circ \approx +40 \text{ kJ mol}^{-1}$   
 non-spontaneous  $\Delta G^\circ$  being positive.

**Remember**  $\Delta G^\circ = \Delta G^\circ_f(\text{products}) - \Delta G^\circ_f(\text{reactants})$

$\Delta G^\circ = -ve$  forward reaction is favoured

$= +ve$  backward reaction is favoured

The positive value of  $\Delta G^\circ$  indicates that the reduction of  $MgO$  with  $C$  does not occur to a significant extent at  $1500^\circ C$ .

14. Metals :  $Na$  (from fused  $NaCl$ ),  $Al$  (from fused  $Al_2O_3 + Na_3AlF_6$ )  
 Non-metals :  $Cl_2$  (from fused  $NaCl$ ),  $F_2$  (from fused  $KHF_2$  in  $HF$ )

- | Oxidising agent                                    | Reducing agent                                              |
|----------------------------------------------------|-------------------------------------------------------------|
| (a) $O_2$ (itself reduced to $O^{2-}$ )            | $S^{2-}$ (in $Cu_2S$ ) oxidised to $SO_2$                   |
| (b) $Cu_2O$ oxidises $S^{2-}$ of $Cu_2S$ to $SO_2$ | reduces $Cu_2O$ to $Cu$ , and itself also reduced to $Cu$ . |



## Extraction of Magnesium

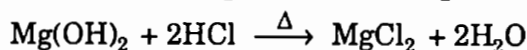
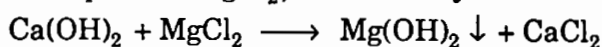
### Occurrence

|            |                                                              |
|------------|--------------------------------------------------------------|
| Magnesite  | : $\text{MgCO}_3$                                            |
| Dolomite   | : $\text{MgCO}_3 \cdot \text{CaCO}_3$                        |
| Kieserite  | : $\text{MgSO}_4 \cdot \text{H}_2\text{O}$                   |
| Epsomite   | : $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$                  |
| Sea water  | : $\text{Mg}^{2+}$ as $\text{SO}_4^{2-}$ and $\text{Cl}^-$   |
| Carnallite | : $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ |

Main sources are **dolomite** and **sea water**.

### Dow Sea-Water Process

Sea water contains about 0.13%  $\text{Mg}^{2+}$  ions, and the extraction of Mg depends on the fact that  $\text{Mg}(\text{OH})_2$  is **very much less soluble than  $\text{Ca}(\text{OH})_2$** . Slaked lime,  $\text{Ca}(\text{OH})_2$  is added to sea water, and calcium ions dissolve and  $\text{Mg}(\text{OH})_2$  is precipitated. This is filtered off, treated with HCl to produce  $\text{MgCl}_2$ , and electrolysed.



The process has been summarised in Fig. 17.6. and 17.7.

### DEEP Focus

The actual electrolyte is a mixture of molten  $\text{NaCl}$ ,  $\text{CaCl}_2$  and  $\text{MgCl}_2$ . This mixture has a lower melting point and higher electrical conductivity than does  $\text{MgCl}_2$  alone, but only  $\text{Mg}^{2+}$  is reduced under the conditions employed in the electrolysis.

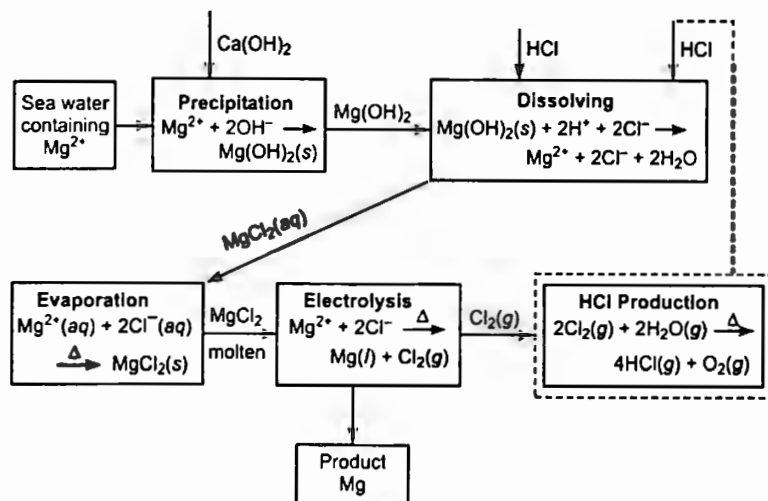
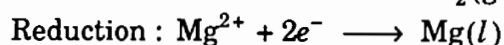
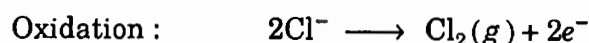


Fig. 17.6 The Dow process for the production of Mg. The main reaction sequence is traced by solid arrows. Recycling of  $\text{Cl}_2(\text{g})$  is shown by broken arrows.

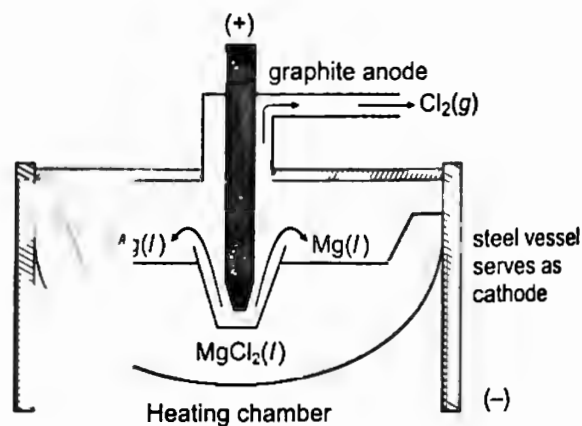


Fig. 17.7 The electrolysis of molten  $\text{MgCl}_2$

## Extraction of Lead

### Occurrence

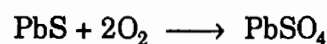
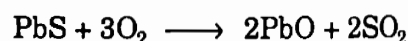
- Galena :  $\text{PbS}$
- Anglesite :  $\text{PbSO}_4$
- Cerussite :  $\text{PbCO}_3$
- Lanakite :  $\text{PbO} \cdot \text{PbSO}_4$
- Matlockite :  $\text{PbCl}_2 \cdot \text{PbO}$

Main source is  $\text{PbS}$ .

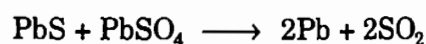
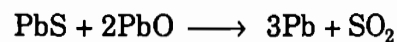
### Self Reduction Method (Air Reduction Process)

**Step I : Concentration by froth flotation process** (Fig 17.5)

**Step II : Roasting** in a limited supply of air :



**Step III : Smelting** is done along with step II. When 50% of the  $\text{PbS}$  has been oxidised, the air supply is cut off and the temperature is increased.  $\text{PbS}$  reduces  $\text{PbO}$  and  $\text{PbSO}_4$  to  $\text{Pb}$  :

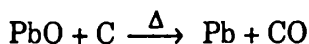


The metal contains a number of metallic impurities  $\text{Cu}$ ,  $\text{Ag}$ ,  $\text{Sn}$ ,  $\text{As}$ ,  $\text{Sb}$ ,  $\text{Bi}$  and  $\text{Zn}$ . These are removed by cooling to near the freezing point of  $\text{Pb}$ , when first  $\text{Cu}$  and then  $\text{Zn}$  containing most of the  $\text{Ag}$  and  $\text{Au}$  solidify (Parkes' method). Preferential oxidation converts  $\text{As}$ ,  $\text{Sb}$  and  $\text{Sn}$  to  $\text{As}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$  and  $\text{SnO}_2$  which float on the surface of the molten metal and may be skimmed off.

Further refining is done by electrolysis.

## Carbon Reduction Process

Roasted ore as obtained in step II above is mixed with coke and melted.



## Extraction of Tin

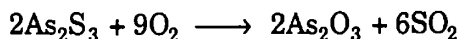
### Occurrence

- Cassiterite (tin stone) :  $\text{SnO}_2$

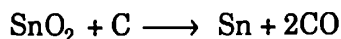
It contains  $\text{FeWO}_4 \cdot \text{MnWO}_4$  (Wolframite) as a magnetic impurity.

**Step I : Concentration** is done in stages :

- **Electromagnetic separation** : To remove magnetic impurities ( $\text{FeWO}_4 \cdot \text{MnWO}_4$ )
- **Gravity separation** : To remove gangue, ore is washed with current of water.
- **Roasting** : To remove volatile impurities as oxides:



**Step II : Reduction (Smelting)** : Concentrated ore from step I is mixed with coal, lime stone and sand and heated in a reverberatory furnace at  $1200^\circ\text{--}1300^\circ\text{C}$



**Step III : Refining** : Sn obtained above has some  $\text{SnO}_2$ . It is refined by :

(i) **Poling** process (molten tin is stirred with poles of green wood which reduces  $\text{SnO}_2$  to Sn).

(ii) **Liquation** (bars of tin are heated on the hearth of a reverberatory furnace when the readily fusible tin flows leaving the impurities like Fe, Cu, W, As etc., (behind).

### Step IV : Electro-refining

Cathode : sheet of pure tin

Anode : blocks of impure tin

Electrolyte : tin sulphate ( $\text{SnSO}_4$ ) in dil.  $\text{H}_2\text{SO}_4$  and some phenol sulphonic acid

Pure tin from the blocks (anode) is deposited at the cathode.

## Extraction of Silver

### Occurrence

- Argentite (silver glance) :  $\text{Ag}_2\text{S}$
  - Horn silver (chlorargyrite) :  $\text{AgCl}$
  - Argentiferous galena :  $\text{PbS} \cdot \text{Ag}_2\text{S}$
  - Pyragyrite or Ruby silver :  $3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$
- Main source is **argentite**.

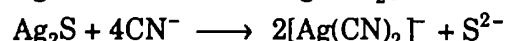
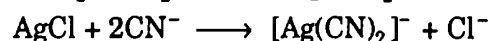
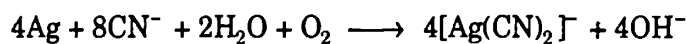
## Cyanide Process

(Based on Hydrometallurgy)

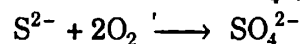
### Mac Arthur —Forrest Method

#### Step I : Complexation of $\text{Ag}/\text{Ag}_2\text{S}/\text{AgCl}$

The powdered ore is treated with  $\text{NaCN}$  solution and  $\text{O}_2$  is bubbled through the solution. Ag if any present in native state is oxidised to  $\text{Ag}^+$ .  $\text{Ag}^+$  is complexed by  $\text{CN}^-$  forming soluble  $[\text{Ag}(\text{CN})_2]^-$

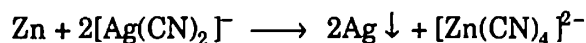


Last reaction is reversible due to very low solubility of  $\text{Ag}_2\text{S}$  in water. Air oxidises  $\text{S}^{2-}$  to  $\text{SO}_4^{2-}$ , S and  $\text{S}_2\text{O}_3^{2-}$



#### Step II : Precipitation of Ag

Zn is added to soluble  $[\text{Ag}(\text{CN})_2]^-$  when Ag is displaced.



#### Step III : Refining by electrolysis

Cathode : pure Ag

Anode : impure Ag

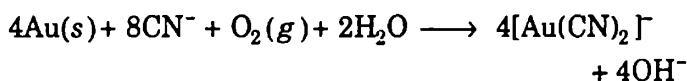
Electrolyte :  $\text{AgNO}_3(\text{aq})$

When electric current is passed, impure Ag (anode) is oxidised to  $\text{Ag}^+$  and is deposited at pure Ag (cathode).

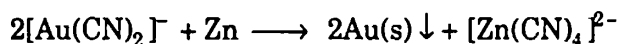
At anode :  $\text{Ag} \longrightarrow \text{Ag}^+ + e^-$

At cathode:  $\text{Ag}^+ + e^- \longrightarrow \text{Ag}$

In case of gold,  $\text{O}_2(g)$  oxidises free metal to  $\text{Au}^+$ , which complexes with  $\text{CN}^-$

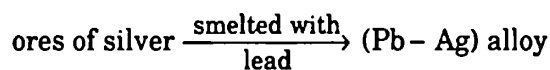


The pure metal is then displaced from the solution by an active metal (as Zn).



## Lead Process

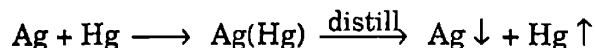
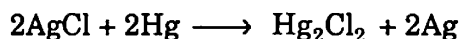
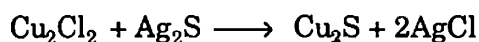
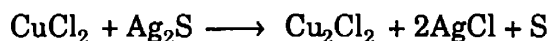
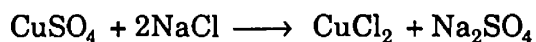
The process depends upon the fact that when ores of silver are smelted down with lead, an alloy of lead and silver is formed; from this alloy lead is removed by oxidation.



- (Pb–Ag) alloy rich in silver : **Cupellation process is used**
- (Pb–Ag) alloy poor in silver : **Parke's or Pattinson process is used**

## Mexican Amalgamation Process

Mercury and magistral (burnt pyrites sulphates and oxides of copper and iron) are added to the powdered mineral containing  $H_2O$  and  $NaCl$ . The mixture is kept for several days. Silver is formed in the amalgam form. On washing, drying and subsequent distillation, silver is obtained.



**Desilverisation of Lead:** When lead-silver alloy is poor in silver (such as argentiferrous lead or galena), desilverisation of lead is affected by **Parke's process**. It depends upon the fact that:

- when zinc is added to a melted alloy of silver and lead, zinc takes away silver from the alloy and itself forms an alloy with silver and not with lead
- alloy of zinc and silver melts at a higher temperature than lead
- the alloy of silver and zinc is lighter than lead and forms two separate layers
- on distillation of silver and zinc alloy, zinc separates

## Pattinson's Process

It depends upon the fact that the alloy of lead and silver containing less than 1.8 per cent of silver, melts at a lower temperature than pure lead. If this type of alloy is melted, and the melted alloy is allowed to cool, lead first separates and repeating the process, one becomes richer in silver. Further recovery is done by cupellation process.

## Extraction of Aluminium

### Occurrence

|            |                                      |
|------------|--------------------------------------|
| Bauxite    | : $Al_2O_3 \cdot 2H_2O$              |
| Kaolin     | : $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ |
| Cryolite   | : $Na_3AlF_6$                        |
| Felspar    | : $K_2O \cdot Al_2O_3 \cdot 6SiO_2$  |
| Corundum   | : $Al_2O_3$                          |
| Orthoclase | : $KAlSi_3O_8$                       |
| Beryl      | : $Be_3Al_2Si_6O_{18}$               |

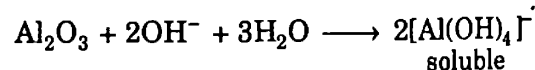
Main source is bauxite.

Felspar or orthoclase on weathering gives rise to porcelain-clay, China-clay or Kaolin.

## Purification of Bauxite

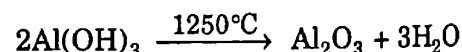
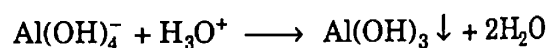
### Baeyer's Process

**Step I :** Bauxite contains  $Fe_2O_3$  and  $TiO_2$  as impurities.  $Al_2O_3$  is amphoteric and dissolves in  $NaOH$ . The other oxides are basic oxides and therefore, insoluble in  $NaOH$ .

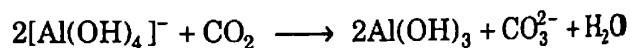


Insoluble oxides (as  $Fe_2O_3$ ) are removed by filtration

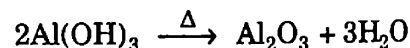
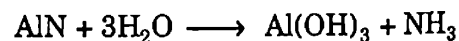
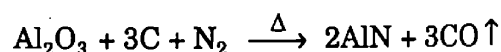
**Step II :** Soluble  $[Al(OH)_4]^-$  is diluted and then acidified when  $Al(OH)_3$  is precipitated which on ignition at  $1250^\circ C$  gives pure alumina :



The complex is decomposed into  $Al(OH)_3$  by passing  $CO_2$  through it



### Serpeck's Process

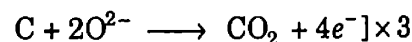


## Electrolysis of $Al_2O_3$ (Hall-Heroult Process)

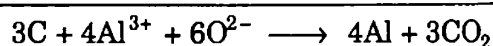
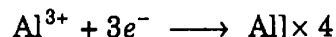
Al is usually extracted by this process.  $Al_2O_3$  is melted with cryolite  $Na_3[AlF_6]$  and electrolysed in a graphite lined steel tank, which serves as cathode. The anodes are also made of graphite. The cell runs continuously and at intervals molten Al (m.p.  $660^\circ C$ ) is drained from the bottom of the cell and more bauxite is added (Fig. 19.8). Cryolite improves the electrical conductivity of the cell as  $Al_2O_3$  is poor conductor. This also serves as an added impurity and lowers the m.p. of the mixture to about  $950^\circ C$ .

Al of 99.6 to 99.8% purity is obtained. Probable net reactions are.

Oxidation at anode:



Reduction at cathode:



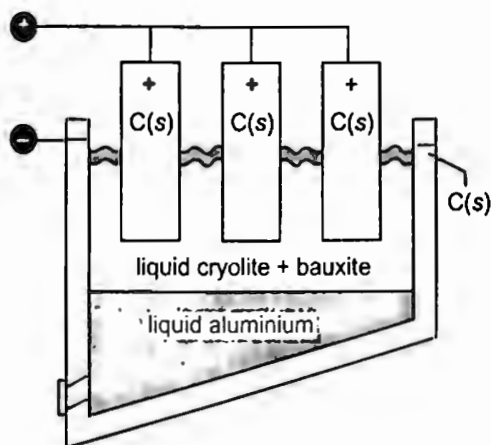
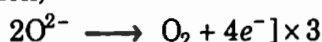


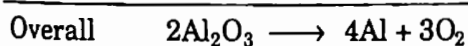
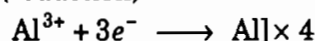
Fig. 17.8 Electrolysis cell for aluminium production. The cathode is a carbon lining in a steel tank. The anodes are also made of carbon. Liquid aluminium is more dense than the electrolyte medium and collects at the bottom of the tank. A crust of frozen electrolyte forms at the top of the cell.

Reaction can also be written as

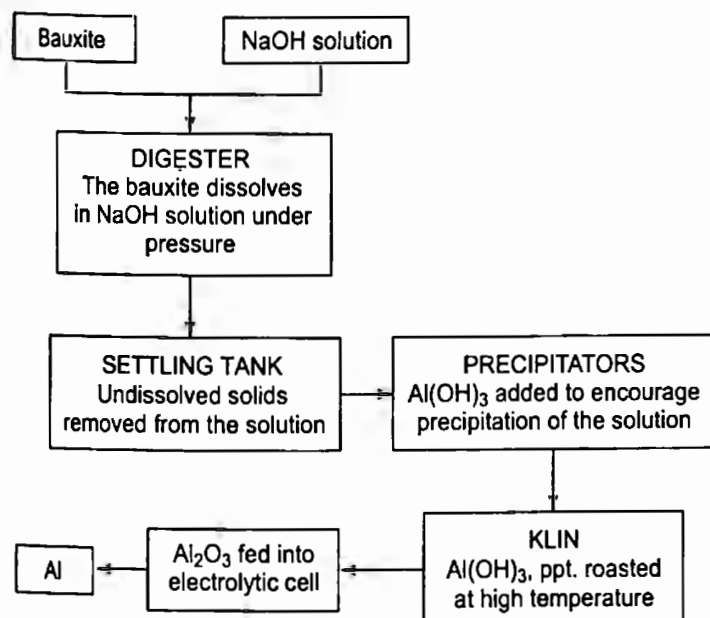
Anode (oxidation)



Cathode (reduction)



Oxygen gas reacts with carbon anodes (at elevated temperature) to form CO



## Extraction of Iron

### Occurrence

|                                      |                                                                                |
|--------------------------------------|--------------------------------------------------------------------------------|
| Haematite                            | : $\text{Fe}_2\text{O}_3$                                                      |
| Magnetite                            | : $\text{Fe}_3\text{O}_4$                                                      |
| Limonite                             | : $\text{FeO}(\text{OH})$ or $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ |
| Siderite                             | : $\text{FeCO}_3$                                                              |
| Pyrites (fool's gold)                | : $\text{FeS}_2$                                                               |
| Pyrrhotite                           | : $\text{FeS}$                                                                 |
| Ilmenite                             | : $\text{FeTiO}_3$                                                             |
| Oxide-ores are main sources of iron. |                                                                                |

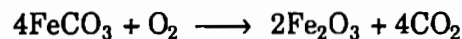
## Carbon Reduction Method

### Step I : Concentration by

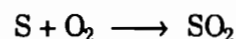
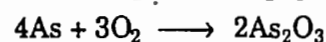
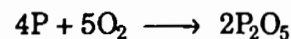
- gravity separation method (which removes gangue)
- magnetic separator (which enriches it by removing non-magnetic impurities)

### Step II : Roasting is done

- to decompose carbonates to  $\text{Fe}_2\text{O}_3$  and also to remove moisture :



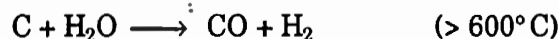
- to oxidise volatile impurities :



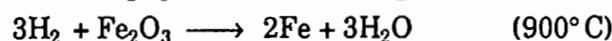
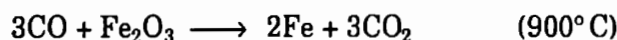
### Step III : Reduction or Smelting

It is done in a blast furnace (Fig. 17.9), the reactions taking place in a blast furnace (along with working temperature) are :

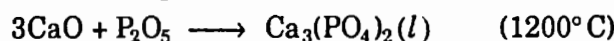
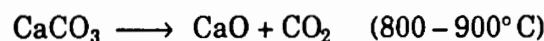
- Formation of reducing agents, principally  $\text{CO}(\text{g})$  and  $\text{H}_2(\text{g})$ :



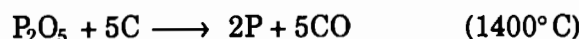
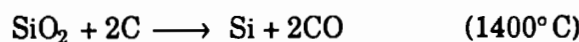
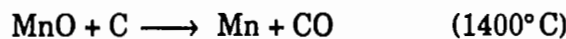
- Reduction of iron oxide :



- Slag formation to remove impurities from ore :

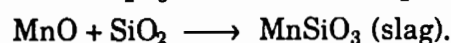
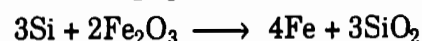


- Impurity formation in iron :



- Iron obtained from a blast furnace is called **pig iron**. It contains about 95% Fe, 4% C and varying quantities of other impurities. **Cast iron** can be obtained by pouring pig iron directly into molds of the desired shape. Cast iron is very hard and brittle and can be used where it will not be subjected to mechanical or thermal shock.

- Wrought iron is prepared by "**Pudding process**" in which cast iron is fused in a reverberatory furnace, the hearth of which is lined with haematite. Reactions taking place are:



• **Pig iron** is converted into steel by following changes :

1. Reduce the carbon content from 3–4% in pig iron to 0–1.5% in steel.
2. Remove, through slag formation, Si, Mn, and P (each present in pig iron to the extent of 1% or so), together with other minor impurities.
3. Add alloying elements (such as Cr, Ni, Mn, V, Mo, and W) to give the steel its desired end properties.

The most important method of steel making today is the **basic oxygen process (BOP)**. The process is carried out in a steel vessel with a refractory lining (usually made of dolomite,  $\text{CaCO}_3 \cdot \text{MgCO}_3$ ). Oxygen gas at about 10 atm pressure and a stream of powdered limestone are fed through a water-cooled lance and discharged above the

molten pig iron. The reactions that occur accomplish the first two objectives are:

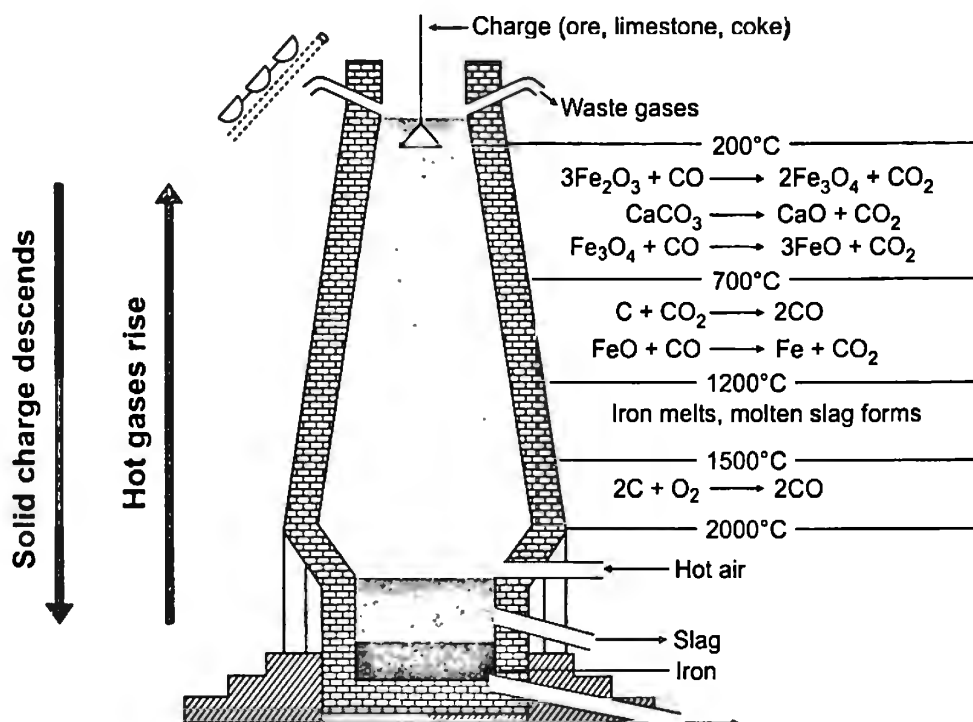
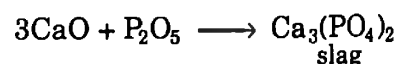
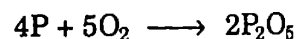
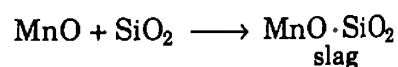
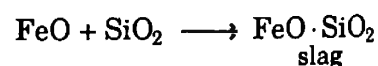
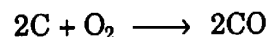
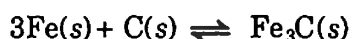


Fig. 17.9 Iron ore, coke, and limestone are added at the top of the furnace, and hot air is introduced through the bottom. Maximum temperatures are attained near the bottom of the furnace where molten iron and slag are drained off.

The properties of steel depend on its chemical composition but also on heat treatment. At high temperatures, iron and carbon in steel combine to form iron carbide,  $\text{Fe}_3\text{C}$ , called cementite:



The forward reaction is endothermic, so that the formation of cementite is favoured at high temperatures. When steel containing cementite is cooled slowly, the above equilibrium shifts to the left, and the carbon separates as small particles of graphite, which give the steel a gray colour. If the steel is cooled rapidly, equilibrium is not attained and the carbon remains large in the form of cementite,  $\text{Fe}_3\text{C}$ . **Steel containing cementite is light in colour, and is harder and more brittle than that containing graphite.**

### DEEP Focus

- Heating the steel to appropriate temperature for a short time and then cooling it rapidly in order to give it the desired mechanical properties is called **tempering**. In this way, the ratio of carbon present as graphite and as cementite can be varied within rather wider limits.

Based on % of carbon, steels are named

| Name        | %C       |
|-------------|----------|
| Mild        | 0.15–0.3 |
| Medium      | 0.3–0.6  |
| High-Carbon | 0.6–0.8  |
| Tool        | 0.5–1.4  |

Table 17.8 shows the composition, properties, and uses of various types of steel.

Table 17.8 Types of Steel

| Composition | Type-mass%            |                              |                                |
|-------------|-----------------------|------------------------------|--------------------------------|
|             | Plain                 | High strength                | Stainless                      |
| C           | 1.35                  | 0.25                         | 0.03-1.2                       |
| Mn          | 1.65                  | 1.65                         | 1.0-10                         |
| P           | 0.04                  | 0.04                         | 0.04-0.06                      |
| S           | 0.05                  | 0.05                         | 0.03                           |
| Si          | 0.06                  | 0.15-0.90                    | 1-3                            |
| Ni          | —                     | 0.4-1.0                      | 1.22                           |
| Cr          | —                     | 0.3-1.3                      | 4.0-27                         |
| Others      | Cu (0.2-0.6)          | Cu (0.01-0.08)               | —                              |
| Uses        | sheet products, tools | construction, steel turbines | kitchen utensils, razor blades |

## Extraction of Zinc

Zinc occurs in the earth's crust to the extent of 132 ppm by weight. It is the twenty-fourth most abundant element.

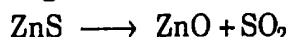
### Occurrence

- Zinc blende (Sphaelerite) :  $(\text{ZnFe})\text{S}$
- Smithsonite (Calamine) :  $\text{ZnCO}_3$
- Hemimorphite :  $\text{Zn}_4(\text{OH})_2(\text{Si}_2\text{O}_7) \cdot \text{H}_2\text{O}$

Main source is zinc blende and is extracted in following steps :

**Step I :** Concentration by froth-flotation process

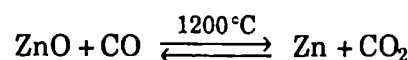
**Step II : Roasting**



$\text{SO}_2$  is the important side product and is used to manufacture  $\text{H}_2\text{SO}_4$ .



**Step III : Reduction of ZnO in a smelter**



Above reaction is reversible and thus high temperature is required to shift the equilibrium towards formation of Zn. Thermodynamically :

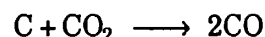
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

To make  $\Delta G^\circ$  negative (for spontaneous reaction)

$$T\Delta S^\circ > \Delta H^\circ \quad \text{and} \quad T > \frac{\Delta H^\circ}{\Delta S^\circ}$$

If we use standard thermodynamic data,  $T$  should exceed  $1200^\circ\text{C}$ . Zn and  $\text{CO}_2$  both are in gaseous state at this temperature. Reversible nature of the above reaction can be minimised :

- (a) by having excess of carbon so that  $\text{CO}_2$  formed is converted to CO



- (b) by cooling the gaseous products so that equilibrium is not attained immediately.

Zinc obtained in this way is of 99% purity.

**Step IV : Refinement by Electrolysis**

ZnO is dissolved in dil.  $\text{H}_2\text{SO}_4$  and electrolysed.

**Anode :** Impure zinc plate

**Cathode :** Pure zinc plate

**Electrolyte :**  $\text{ZnSO}_4/\text{H}_2\text{SO}_4$

Zinc from impure zinc plate is oxidised at anode, goes into solution and reduced to pure zinc at cathode.

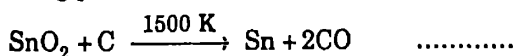
**Anode :**  $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2e^-$

**Cathode :**  $\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$

## Target Practice 2

1. Sulphide ore is concentrated by the method .....

2. Name the following process



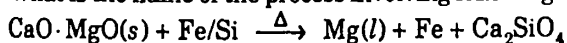
3. Ag is precipitated when Zn is added to  $[\text{Ag}(\text{CN})_2]^-$ . Write the reaction. ....

4. In the extraction of silver, some lead is also present as impurity in final step. This lead can be removed by

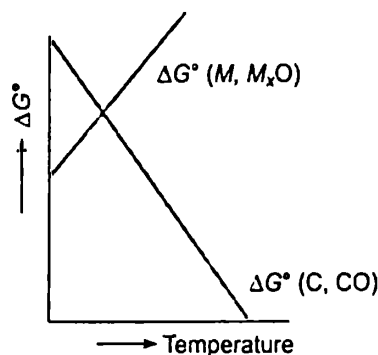
(i) ..... (ii) .....

5. Carbon can't be used to reduce  $\text{Al}_2\text{O}_3$  to Al while ZnO can be reduced by carbon. It is due to .....

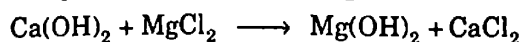
6. What is the name of the process involving following reaction :



7. Based on following Ellingham diagram, indicate the temperature favourable for the reduction of metal oxide to metal.



8. What is the principle of the following reaction?



9. Alumina (
- $\text{Al}_2\text{O}_3$
- ) and silica (
- $\text{SiO}_2$
- ) get dissolved in a concentrated solution of NaOH under pressure.

(a) In what forms are these soluble? Write reactions.

(b)  $\text{Al(OH)}_3$  is precipitated when  $\text{CO}_2$  is passed or by seeding with some freshly precipitated  $\text{Al(OH)}_3$ . Explain.

(c) Is silica precipitated by treatment in (b).

10. Match the following properties of Al with the uses to which the metal or its compounds are put.

- |                                               |                                  |
|-----------------------------------------------|----------------------------------|
| (i) Good thermal conductivity                 | (a) Building ships and aircrafts |
| (ii) Good electrical conductivity             | (b) Utensils                     |
| (iii) Low density and resistance to corrosion | (c) Electric wires               |
| (iv) Non-toxicity                             | (d) Adsorbent                    |
| (v) Gel nature of $\text{Al(OH)}_3$           | (e) Food-packaging               |

11. In the production of iron, intermediate are oxides. Name the oxides of iron

(a) ..... (b) .....

12. Basic impurities are removed as slag in the production of iron. Write various formulae of slags.

(a) ..... (b) .....  
(c) .....

## Answers

- Froth flotation process
- Smelting (reduction)
- $2[\text{Ag(CN)}_2]^- + \text{Zn} \longrightarrow [\text{Zn(CN)}_4]^{2-} + 2\text{Ag}$
- (i) Cupellation process if rich in silver  
(ii) Parke's or Pattinson process is used.
- Al has greater reactivity with oxygen hence, can't be reduced by carbon
- Pidgeon process.
- The formation of carbon monoxide from carbon can reduce the metal oxide to metal at a temperature higher than the point of intersection of the two lines.  
(To make  $\Delta G = -ve$ ,  $T\Delta S > \Delta H$ )  
Sine  $\Delta G = \Delta H - T\Delta G$

- Solubility of  $\text{Mg(OH)}_2$  is lower than that of  $\text{Ca(OH)}_2$ .
- (a)  $\text{Al}_2\text{O}_3 + 2\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow 2\text{NaAl(OH)}_4$   
 $\text{SiO}_2 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}$   
(b)  $2\text{NaAl(OH)}_4 + \text{CO}_2 \longrightarrow 2\text{Al(OH)}_3 \downarrow + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$   
(c) Silica is more acidic oxide than alumina hence, silicate remains in solution.
- (i) (b) (ii) (c) (iii) (a) (iv) (e) (v) (d)
- (a) FeO (b)  $\text{Fe}_2\text{O}_3$  (c)  $\text{Fe}_3\text{O}_4$
- (a)  $\text{CaSiO}_3$  (b)  $\text{MgSiO}_3$  (c)  $\text{MnSiO}_3$

## Practice Exercise 2

- Pb can also be obtained by reduction of roasted ore with coke. Outline the process.
- Considering 100% pure, which of the following has maximum percentage of Pb?  
(a) PbS (b)  $\text{PbSO}_4$   
(c)  $\text{PbCO}_3$  (d)  $\text{PbO} : \text{PbSO}_4$
- $\text{SnO}_2$  can be precipitated as  $\text{Sn(OH)}_4$ . Can this be used to concentrate tin stone.
- (A) Tin stone is amphoteric. Explain.  
(B)  $\text{SnO}_2$  is reduced to metallic Sn on smelting oxide with anthracite, limestone and sand.  
In this, function of sand is:  
(a) it acts as a flux  
(b) it removes basic impurities as slag  
(c) both (a) and (b) are correct  
(d) none of the above is correct  
(C) Which is not the correct process-mineral matching in metallurgical extraction?  
(a) Leaching : Ag  
(b) Zone-refining : Sn  
(c) Liquation : Sn  
(d) van Arkel : Zr

- Scrap tin plate can be recycled by dissolving the tin in NaOH solution, followed by electrolysis. Write equations for the reactions involved.
- To prevent the air oxidation of aqueous solutions of  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$ , sometimes metallic tin is kept in contact with the  $\text{Sn}^{2+}$ . Suggest how this helps to prevent the oxidation?
- Gold is also extracted by cyanide process as in case of silver. Outline the reactions.
- When 1 mol of pure  $\text{Ag}_2\text{CO}_3$  is strongly heated, calculate weight of residue obtained.
- How is Ag extracted from silver coin?
- (Ag + Pb) alloy  $\xrightarrow{\text{melt and add zinc}}$  (Ag + Pb + Zn) melt

|                    |         |
|--------------------|---------|
| Cool $\rightarrow$ | Layer X |
|                    | Layer Y |

Select correct statement based on above scheme:

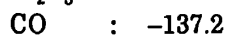
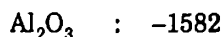
- Layer X contains zinc and silver
- Layer Y contains lead and silver but amount of silver in this layer is smaller than in the layer X.
- X and Y are immiscible layers
- All of the above are correct statements

11. In the purification of bauxite ore as preliminary step in the production of Al,  $[\text{Al}(\text{OH})_4]^-$  can be converted to  $\text{Al}(\text{OH})_3$  by passing  $\text{CO}_2$  through it. Write an equation for the reaction that occurs.

12. Addition of  $\text{NH}_4\text{Cl}$  can also precipitate  $\text{Al}(\text{OH})_3$  from soluble  $\text{Na}[\text{Al}(\text{OH})_4]$ . Explain.

13. Coke does not cause reduction of  $\text{Al}_2\text{O}_3$ . Explain.

$\Delta G_f^\circ$  (in  $\text{kJ mol}^{-1}$ ) for



14. What happens when  $\text{Al}(\text{NO}_3)_3$  is heated?

15. In the **Baeyer's process**:

(a)  $\text{Al}_2\text{O}_3$  goes into solution as soluble  $[\text{Al}(\text{OH})_4]^-$  while other basic oxides as  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  remain insoluble.

(b)  $\text{Al}_2\text{O}_3$  changes to  $\text{AlN}$  which in turn decomposed by  $\text{H}_2\text{O}$

(c)  $\text{Al}_2\text{O}_3$  changes to  $\text{Al}_2(\text{CO}_3)_3$  which changes to  $\text{AlCl}_3$

(d) none of the above is correct

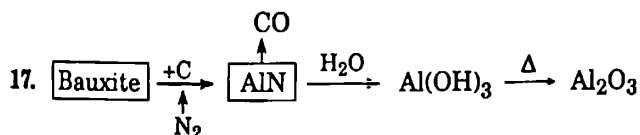
16. In electrolysis of  $\text{Al}_2\text{O}_3$  by Hall-Heroult process:

(a) Cryolite  $\text{Na}_3[\text{AlF}_6]$  lowers the melting point of  $\text{Al}_2\text{O}_3$  and increases its electrical conductivity.

(b) Al is obtained at cathode and probably  $\text{CO}_2$  at anode

(c) both (a) and (b) are correct

(d) none of the above is correct



This flow-sheet is for

(a) Baeyer's process (b) Serpeck's process

(c) Hall's process (d) Kroll's process

18. Which mineral has been named incorrectly?

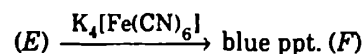
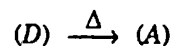
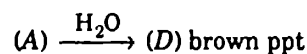
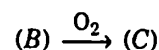
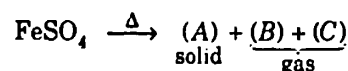
(a) Bauxite :  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$

(b) Corundum :  $\text{Al}_2\text{O}_3$

(c) Cryolite :  $3\text{NaF} \cdot \text{AlF}_3$

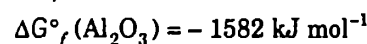
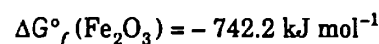
(d) Felspar :  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$

19. Identify (A) to (F) in the following :



20. It is possible to identify an "Iron cycle" of the same kind as a water or nitrogen cycle. Suggest some stages in the cycle.

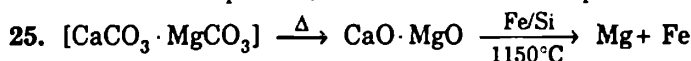
21. Al is costlier than Fe but Al is sacrificed to convert  $\text{Fe}_2\text{O}_3$  into Al. Why this change is possible? Name this process.



22. When iron ore is reduced in a blast furnace, some of the  $\text{SiO}_2$  impurity is also reduced by reaction with carbon to give elemental silicon and carbon monoxide. The silicon is subsequently reoxidised in basic oxygen process, and the resulting  $\text{SiO}_2$  reacts with  $\text{CaO}$ , yielding slag, which is then separated from the molten steel. Write balanced equations for the three reactions involving  $\text{SiO}_2$ .

23. Although iron is only about two-third as abundant as aluminium in Earth's crust, mass for mass it costs only about one-quarter as much to produce. Why?

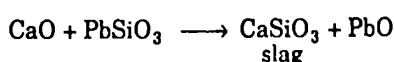
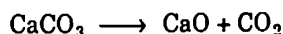
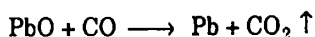
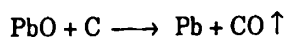
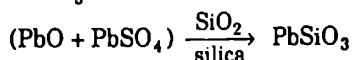
24. Dolomite ( $\text{MgCO}_3 \cdot \text{CaCO}_3$ ) can also be treated to get  $\text{MgCl}_2$  which in turn is electrolysed to get Mg. (Dow natural brine process). Give reactions of this process



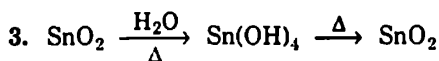
Name this process.

## Answers

1.  $\text{PbS} \xrightarrow[\text{O}_2]{\text{roasting}} \text{PbO}, \text{PbSO}_4$ . This mixture is smelted with coke,  $\text{SiO}_2$  and  $\text{CaCO}_3$

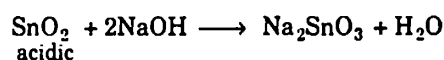
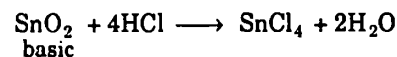


| Ore                                  | % of Pb         |
|--------------------------------------|-----------------|
| (a) PbS                              | 86.55 (maximum) |
| (b) $\text{PbSO}_4$                  | 68.21           |
| (c) $\text{PbCO}_3$                  | 77.44           |
| (d) $\text{PbO} \cdot \text{PbSO}_4$ | 78.62           |

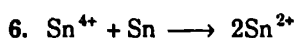
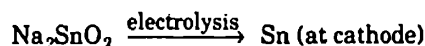
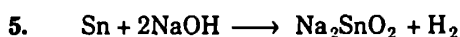


This process will not precipitate impurities hence, precipitation of  $\text{Sn}(\text{OH})_4$  and subsequent heating will enrich  $\text{SnO}_2$ .

4. (A)  $\text{SnO}_2$  is soluble in acid and alkali both hence, amphoteric.



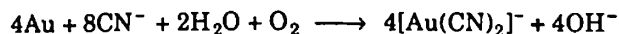
(B) (c) (C) (b)



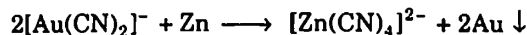
Sn reduces  $\text{Sn}^{4+}$  to  $\text{Sn}^{2+}$ .



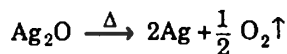
7. In the cyanide process, crushed rock containing traces of gold is treated with 0.1–0.2% solution of NaCN and aerated.  $O_2$  (air) oxidises free metal to  $Au^+$  which complexes with  $CN^-$



The pure metal is displaced from solution by an active metal.



8.  $Ag_2CO_3 \xrightarrow{\Delta} Ag_2O + CO_2 \uparrow$



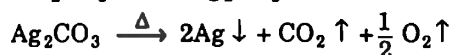
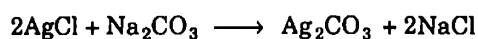
Residue is metallic Ag.

$$\begin{aligned} 1 \text{ mol } Ag_2CO_3 &= 2 \text{ mol Ag} \\ &= 216 \text{ g Ag} \end{aligned}$$

9. Silver coin (Cu + Ag)  $\xrightarrow{\text{conc. } HNO_3}$   $(Cu^{2+} + Ag^+) NO_3^-$



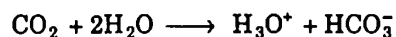
$AgCl \downarrow$  (white ppt)



Or use cyanide process with  $AgCl$ .

10. (d)

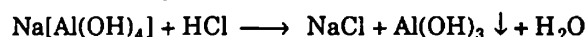
11. Aqueous solution of  $CO_2$  is acidic. Hence,  $CO_2$  when passed into  $[Al(OH)_4]^-$  solution makes it acidic hence,  $Al(OH)_3$  is precipitated.



12.  $NH_4Cl$  solution is acidic due to hydrolysis :



hence addition of  $NH_4Cl$  solution precipitates  $Al(OH)_3$  when added to  $NaAl(OH)_4$



13.  $Al_2O_3 + C \longrightarrow 2Al + 3CO$

$$\Delta G^\circ = 3\Delta G_f^\circ(CO) - \Delta G_f^\circ(Al_2O_3)$$

$$= -3(137.2) + 1582$$

$$= +ve$$

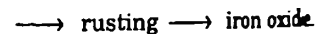
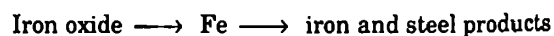
hence, reaction is not spontaneous.

14.  $2Al(NO_3)_3 \xrightarrow{\Delta} Al_2O_3 + 6NO_2 + 1.5O_2$

15. (a) 16. (c) 17. (b) 18. (d)

19. (A) :  $Fe_2O_3$  (B) :  $SO_2$  (C) :  $SO_3$  (D) :  $Fe(OH)_3$  (E) :  $FeCl_3$  (F) :  $KFe^{III}[Fe^{II}(CN)_6]$ , Prussian blue.

20. The cycle might be :



21.  $2Al + Fe_2O_3 \longrightarrow 2Fe + Al_2O_3$

$$\Delta G^\circ = \Delta G_f^\circ(Al_2O_3) - \Delta G_f^\circ(Fe_2O_3)$$

$$= -1582 + 742.2$$

$$= -ve$$

hence, this reduction of  $Fe_2O_3$  by Al is possible. This is called **Thermite welding**.

## DEEP Focus

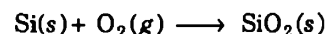
Remember:

$$* \Delta G^\circ = \Delta G_f^\circ(\text{products}) - \Delta G_f^\circ(\text{reactants})$$

$$* \Delta G^\circ = +ve, \text{ then backward reaction}$$

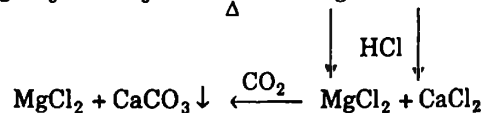
$$= -ve, \text{ then forward reaction}$$

22.  $SiO_2(s) + 2C(s) \longrightarrow Si(s) + 2CO(g)$



23. Iron production does not require electrolysis.

24.  $MgCO_3 \cdot CaCO_3 \xrightarrow[\Delta]{\text{calcination}} MgO + CaO + 2CO_2 \uparrow$



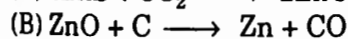
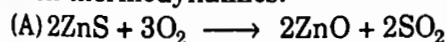
[On passing  $CO_2$  into aq  $MgCl_2$  and  $CaCl_2$  solution,  $CaCO_3$  is precipitated leaving  $MgCl_2$  soluble].

25. It is called Pidgeon process.

# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** Following method of extracting Zn is based on thermodynamics:



$\Delta G^\circ_f$  (standard free energies of formation, in  $\text{kJ mol}^{-1}$ ) of

$$ZnS = -205.4; \quad ZnO = -318.2$$

$$SO_2 = -300.4; \quad CO = -137.3$$

Calculate free energy changes of the above reactions and comment on the result.

**Solution** For reaction (A)

$$\begin{aligned} \Delta G^\circ &= 2\Delta G^\circ_f(ZnO) + 2\Delta G^\circ_f(SO_2) - 2\Delta G^\circ_f(ZnS) \\ &= 2[-318.2 - 300.4 + 205.4] \\ &= -826.4 \text{ kJ} \quad (\Delta G^\circ_f(\text{element}) = 0) \end{aligned}$$

For reaction (B)

$$\begin{aligned} \Delta G^\circ &= \Delta G^\circ_f(CO) - \Delta G^\circ_f(ZnO) \\ &= -137.3 + 318.2 \\ &= +180.9 \text{ kJ} \end{aligned}$$

For reaction (A),  $\Delta G^\circ$  is negative hence, reaction is spontaneous; reaction (B) is non-spontaneous  $\Delta G^\circ$  being positive for it.

### DEEP Focus

Again remember :

\*  $\Delta G^\circ = \Delta G^\circ_f(\text{products}) - \Delta G^\circ_f(\text{reactants})$

\*  $\Delta G^\circ = +ve$  indicates non-spontaneous reaction (in forward direction)

\*  $\Delta G^\circ = -ve$  indicates spontaneous reaction (in forward direction)

**Problem 2.** Explain the difference between hydro-metallurgy and pyro-metallurgy.

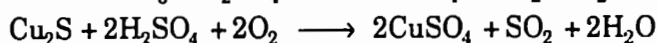
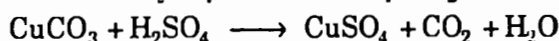
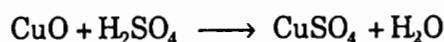
**Solution** The metallurgical procedure based on the roasting of an ore, followed by its reduction (usually with carbon), is known as **pyro-metallurgy**. A key consideration in pyro-metallurgy is the temperature at which reaction becomes spontaneous. As the term "**pyro**" suggests, often this temperature is quite high. Some of the characteristics of this process are :

- large quantities of waste material generated in concentrating low grade ores;
- high energy consumption to maintain high temperatures necessary for roasting and reduction of ores;
- gaseous emissions, such as  $SO_2$  in roasting, that must be controlled.

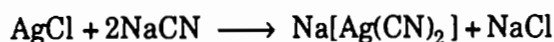
In **hydro-metallurgy**, the materials handled are water and aqueous solutions at moderate temperatures rather than dry materials at high temperatures. It involves :

- leaching with acid/water;
- purification and/or concentration;
- precipitation.

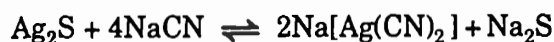
Low grade oxide, carbonate and sulphide ores of copper are treated with dilute sulphuric acid in the presence of oxygen :



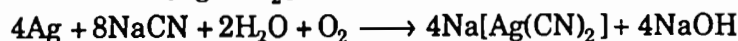
When the silver ore,  $AgCl$ , is treated with an aqueous solution of sodium cyanide,  $AgCl$  dissolves in it due to the formation of  $Na[Ag(CN)_2]$  :



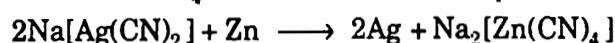
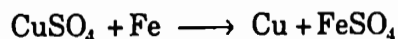
Sulphide ore,  $Ag_2S$ , dissolves only slowly as the reaction is reversible :



If air is passed through this solution, sodium sulphide is oxidised to sodium sulphate and the forward reaction goes to completion dissolving all the sulphide ore. In the presence of air, native silver is also leached out in the form of  $Na[Ag(CN)_2]$

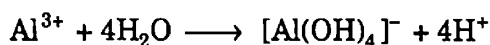


The leached out metals are recovered from the solution either by precipitation on treatment with a more electropositive metal or by electrolysis. For example, copper can be recovered from its solution by adding metals like Fe, Al, etc. Silver is obtained from its solution by treatment with Zn or Al :

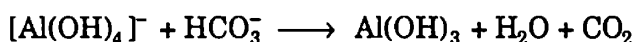


**Problem 3.** In some foam-type fire extinguishers, the reactants are  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{NaHCO}_3$  solutions. When the extinguisher is activated, these reactants are allowed to mix, producing  $\text{Al}(\text{OH})_3$  and  $\text{CO}_2$ . The  $\text{Al}(\text{OH})_3$ — $\text{CO}_2$  foam extinguishes the fire. Write the net ionic equation to represent this reaction.

**Solution**  $\text{Al}_2(\text{SO}_4)_3$  solution is acidic due to hydrolysis :



$[\text{Al}(\text{OH})_4]^-$  reacts with  $\text{HCO}_3^-$  forming  $\text{Al}(\text{OH})_3$ — $\text{CO}_2$  foam :

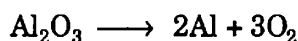


**Problem 4.** Use the relationship  $\Delta G^\circ = -nFE^\circ_{\text{cell}}$  to estimate the minimum voltage required to electrolyse  $\text{Al}_2\text{O}_3$  in the Hall-Heroult process.

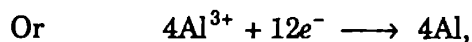
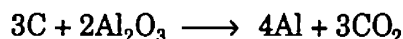
$$\Delta G^\circ_f (\text{Al}_2\text{O}_3) = -1520 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ_f (\text{CO}_2) = -394 \text{ kJ mol}^{-1}$$

Show that the oxidation of the graphite anode to  $\text{CO}_2$  permits the electrolysis to occur at a lower voltage than if the electrolysis reactions were



**Solution** Net reaction in Hall-Heroult process is:



Number of electrons ( $n$ ) = 12,  $\Delta G^\circ_f (\text{element}) = 0$

$$\Delta G^\circ = 3\Delta G^\circ_f (\text{CO}_2) - 2\Delta G^\circ_f (\text{Al}_2\text{O}_3)$$

$$= -3 \times 394 - 2(-1520)$$

$$= 1858 \text{ kJ}$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$-E^\circ_{\text{cell}} = \frac{\Delta G^\circ}{nF} = \frac{1858 \times 1000}{12 \times 96500}$$

$$= 1.60 \text{ V}$$

For the reaction  $\text{Al}_2\text{O}_3 \longrightarrow 2\text{Al} + 3\text{O}_2$

$$\Delta G^\circ = 1520 \text{ kJ}$$



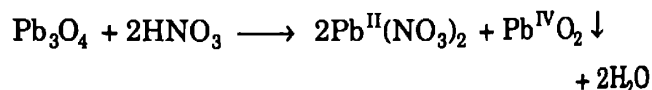
$$\therefore -E^\circ_{\text{cell}} = \frac{\Delta G^\circ}{nF} = \frac{1520 \times 1000}{6 \times 96500}$$

$$= 2.62 \text{ V}$$

Thus Hall-Heroult process takes place at lower voltage.

**Problem 5.** The names dlead (II) lead (IV) oxide and plumbous orthoplumbate have been used to describe red lead  $\text{Pb}_3\text{O}_4$ . Show that these names are true.

**Solution** When  $\text{Pb}_3\text{O}_4$  is treated with  $\text{HNO}_3$ ,  $\text{Pb}(\text{NO}_3)_2$  is formed and  $\text{PbO}_2$  is precipitated :



This shows that red lead has  $\text{PbO}$  and  $\text{PbO}_2$  in 2 : 1 molar ratio and thus it is  $2\text{PbO} \cdot \text{PbO}_2$  and is thus dlead (II) lead (IV) oxide. Only  $\text{PbO}$  reacts with  $\text{HNO}_3$  forming  $\text{Pb}(\text{NO}_3)_2$  while  $\text{PbO}_2$  remains unreacted and is precipitated.

**Problem 6.** The following are two reaction schemes involving Mg.

**Scheme I**  $\text{Mg} \xrightarrow{\text{air } \Delta} \text{colourless solid A} \xrightarrow{\text{HCl}}$

$\text{colourless solution B} \xrightarrow{\text{Na}_2\text{CO}_3} \text{white ppt C}$

$\text{white ppt F} \xleftarrow{\text{Ca}(\text{OH})_2} \text{colourless gas E} \xleftarrow{\Delta} \text{D}$

**Scheme II**  $\text{Mg} \xrightarrow{\text{dil. H}_2\text{SO}_4} \text{colourless solution G} \xrightarrow{\text{NaOH}}$

$\text{white ppt H} \xrightarrow{\text{HNO}_3} \text{colourless solution}$

$\text{D} + \text{O}_2 + \text{gas J} \xleftarrow{\Delta} \text{I} \xleftarrow{\text{evaporate}}$

Identify A to J

**Solution** A :  $\text{MgO}$ ; B :  $\text{MgCl}_2$ ; C :  $\text{MgCO}_3$ ;  
D :  $\text{MgO}$ ; E :  $\text{CO}_2$ ; F :  $\text{CaCO}_3$ ;  
G :  $\text{MgSO}_4$ ; H :  $\text{Mg}(\text{OH})_2$ ;  
I :  $\text{Mg}(\text{NO}_3)_2$  J :  $\text{NO}_2$

**Problem 7.** Explain following terms

- Electrometallurgy
- Zone refining
- van Arkel de-Boer process
- Mond's process

**Solution**

(a) **Electrometallurgy**

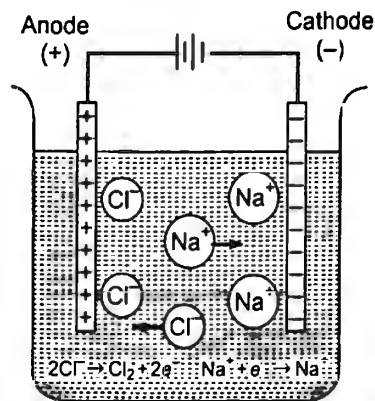
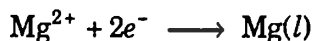
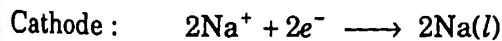
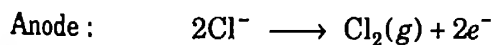
The two metallurgical processes, namely pyrometallurgy and hydrometallurgy can be used in the extraction of a fairly large number of metals. These methods, however, cannot be used in cases:

Where the metal is highly reactive, e.g., Na, Li, etc. There are no any chemical-reducing agent strong enough to prepare these metals.

Where the oxide gets reduced only at very high temperature at which formation of carbides also takes place, e.g., Al, Mg, etc.

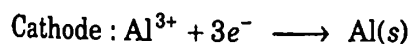
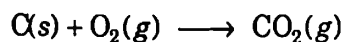
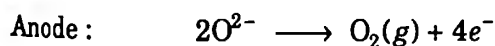
In these cases, metals can be extracted by electrolysis of their salts in molten state. Thus, sodium and magnesium are prepared by electrolysis of fused chlorides, where the

metals are liberated at the cathode and chlorine gas is evolved at the anode. Following reactions take place during electrolysis :



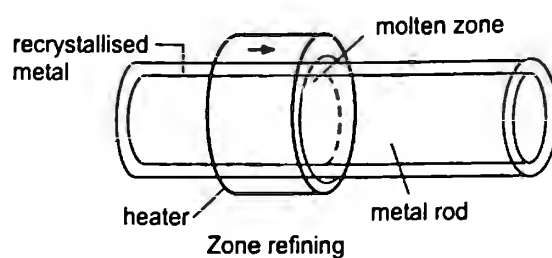
Electrolysis of molten sodium chloride

In theory, aluminium metal could be made the same way. But, aluminium trichloride is covalent and it does not conduct electricity. Aluminium is obtained by electrolytic reduction of alumina in fused cryolite at 1100–1300 K using carbon anode and iron cathode. Electrolysis yields aluminium at cathode and  $\text{O}_2$  at anode which reacts with carbon to produce  $\text{CO}_2$ . The reactions at electrodes are :



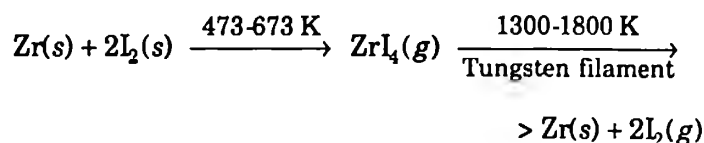
### (b) Zone Refining

This method is used to obtain metals of very high purity. The basic principle involved in this process is similar to fractional crystallisation. A small heater is used to heat a bar of the impure metal. The heater melts a small band of metal as it is slowly moved along the rod. As small bands of metal are thus melted sequentially, the pure metal crystallises out of the melt, while impurities pass into the adjacent molten zone. The impurities thus collect at the end of the bar. This end can be cut off and removed. High grade germanium and the silicon are obtained by purifying them by zone refining.

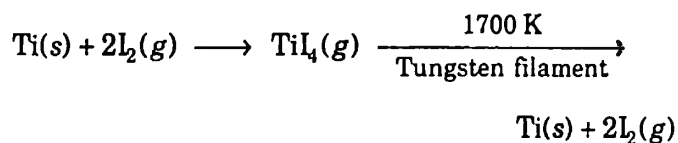


### (c) van Arkel de-Boer Process

This method is based on the thermal decomposition of a volatile metal compound like an iodide. In this method, first a metal iodide is formed by direct reaction of iodine and the metal to be purified at a temperature of 475–675 K in an evacuated vessel. The vapours of metal iodide, thus formed are heated strongly on a tungsten or tantalum filament at 1300–1800 K. The metal iodide decomposes to yield the pure metal, as in the case of zirconium.



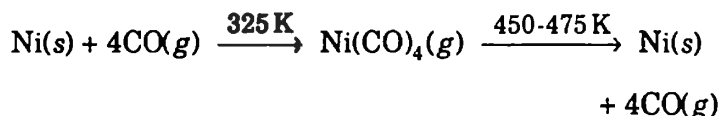
Titanium is also purified by this method. The impure metal is heated with iodine and  $\text{TiI}_4$  thus formed is decomposed by heating at 1700K over tungsten filament.



The regenerated iodine is used over and over again. This process is very expensive and is employed for the preparation of limited amounts of very pure metals for special uses.

### (d) Mond Process

Some metals are purified by obtaining their volatile carbonyl compounds which on heating strongly decompose to yield pure metal. Purification of nickel is done by this method. Impure nickel is reacted with carbon monoxide at 325 K to give volatile nickel carbonyl leaving solid impurities behind. Pure nickel is obtained by heating nickel carbonyl at 450–475 K.

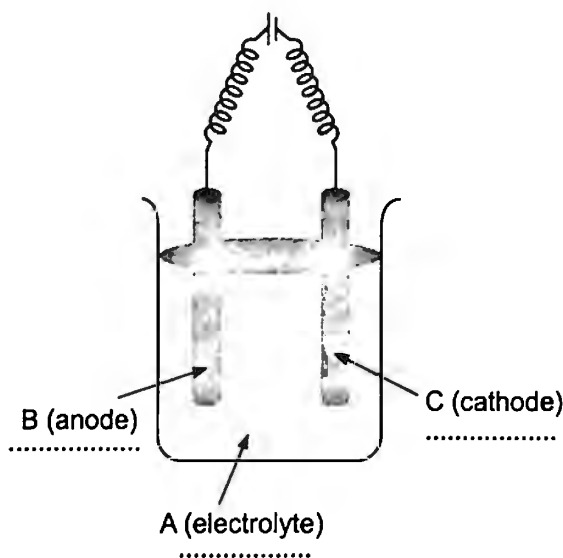


# Master Exercises

## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

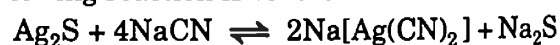
- Is it possible to reduce a sulphide ore directly with carbon.
- Consider following reactions
  - $2\text{ZnS} + 3\text{O}_2 \longrightarrow 2\text{ZnO} + 2\text{SO}_2$   
 $\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}$
  - $2\text{ZnS} + \text{C} \longrightarrow 2\text{Zn} + \text{CS}_2$ 
    - Which reaction is more spontaneous?
    - Which reaction has more negative value of  $\Delta G$ ?
    - Which reaction has more positive value of  $\Delta G$ ?
- Which reactions are favourable?
  - $\text{MgO} + \text{Si} \longrightarrow$
  - $\text{SiO}_2 + \text{Mg} \longrightarrow$
- Specify magnetic impurity present in tin stone .....
- Pure tin is obtained by electro-refining. Specify the indicated (by arrow) contents.



- The recovery of silver from the solutions used in developing and fixing photographic film and prints presents just such a problem. Silver is an expensive metal, and the recovery is profitable. Moreover, if not recovered, the silver ions would constitute and undesirable pollutant in water supplies.

- In what form is silver present in the solutions after developing and fixing photographic film?
- How is silver recovered from such solution?
- What is undesirable pollutant?

- Following reaction is reversible



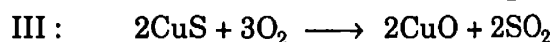
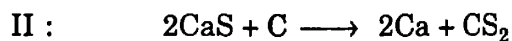
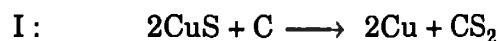
Suggest a method to make it spontaneous.

- ZnS is always contaminated with PbS. Outline a method that can enrich PbS by froth flotation process.
- Consider following facts
  - Zinc and lead are immiscible in molten state; zinc is lighter than lead.
  - Solubility of silver in molten zinc is higher than that in molten lead.
  - Zinc is volatile.
  - Outline method of separation of silver from lead based on above facts.
  - Name the method
- Write full form of BOP process of making steel.
  - Write various forms of iron.
  - Which is the purest form?
- Consider following equilibrium
 
$$3\text{Fe}(s) + \text{C}(s) \rightleftharpoons \text{Fe}_3\text{C}(s), \quad \Delta H^\circ > 0$$

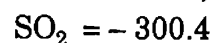
What is the effect of temperature on this equilibrium?

### Analytical Questions

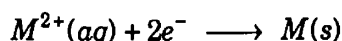
- Calculate the free energy changes for these reactions



Given  $\Delta G^\circ_f$  (in  $\text{kJ mol}^{-1}$ ) for



- (b) Which of them are spontaneous under standard conditions?
- (c) What do you notice about the value of  $\Delta G_f^\circ(\text{CS}_2)$  compared to  $\Delta G_f^\circ(\text{SO}_2)$ ?
- (d) Why are the reactions not carried out at standard conditions?
2. A student suggested that calcium should be made if calcium oxide is reacted with aluminium powder. Was the student correct?
- $\Delta G_f^\circ(\text{CaO}) = -604.2 \text{ kJ mol}^{-1}$   
 $\Delta G_f^\circ(\text{Al}_2\text{O}_3) = -1582 \text{ kJ mol}^{-1}$
3. Although Au is soluble in aqua regia, Ag is not. What is the likely reason for this difference?
4.  $\text{FeCr}_2\text{O}_4$  (chromite) can be used to extract Cr. Outline scheme of extraction.
5. Lead metal is purified by electrolysis in a manner similar to that for copper; the electrolyte is lead (II) hexafluorosilicate  $\text{PbSiF}_6$ . Describe the process.
6. (a) Pure iron is prepared for special purposes by precipitating iron (III) oxide and reducing the dry oxide with  $\text{H}_2$  gas. Write the balanced equation.  
 (b)  $\text{HCl}$  can't be used to precipitate  $\text{Al}(\text{OH})_3$  from soluble  $\text{Na}[\text{Al}(\text{OH})_4]$  but addition of  $\text{NH}_4\text{Cl}$  can cause precipitation. Explain by reactions.  
 (c)  $\text{AgCl}$  (Horn silver) is converted into Ag by pyrometallurgical method. Describe reactions.
7. Zinc, cadmium and mercury are found in nature as sulphides. Values of standard reduction potentials for the half-reactions are :



| M  | $E^\circ$ |
|----|-----------|
| Zn | -0.76 V   |
| Cd | -0.40 V   |
| Hg | +0.79 V   |

Explain, why roasting of  $\text{ZnS}$  gives  $\text{ZnO}$  but roasting of  $\text{HgS}$  gives elemental Hg. What product would you expect from roasting  $\text{CdS}$ ?

8. When an inert atmosphere is needed for a metallurgical process, nitrogen is frequently used. However, in the reduction of  $\text{TiCl}_4$  by magnesium, helium is used. Explain, why nitrogen is not suitable for this process?
9. The following equations represent reactions used in some important metallurgical processes:
- (a)  $\text{Fe}_3\text{O}_4 + \text{CO}(\text{g}) \longrightarrow \text{Fe}(\text{l}) + \text{CO}_2(\text{g})$   
 (b)  $\text{MgCO}_3(\text{s}) + \text{SiO}_2(\text{s}) \longrightarrow \text{MgSiO}_3(\text{l}) + \text{CO}_2(\text{g})$   
 (c)  $\text{Au}(\text{s}) + \text{CN}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \longrightarrow$   
 $[\text{Au}(\text{CN})_2]^- (\text{aq}) + \text{OH}^-(\text{aq})$

Balance the equations. Which one (s) represent reduction to a free metal?

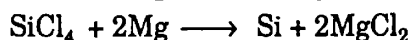
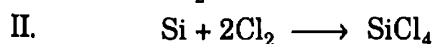
10. Assuming complete recovery of metal, which of the following ores would yield the greater quantity of copper on a mass basis?
- (a) an ore containing 3.30% (by mass) azurite  $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$  or  
 (b) an ore containing 4.95% (by mass) chalcopyrite  $\text{CuFeS}_2$ .
11. When 1.164 g of a certain metal sulphide was roasted in air, 0.972 g of the metal oxide was formed. If the oxidation number of the metal is +2, calculate the molar mass of the metal.
12. How much aluminium can be produced by a current of 94.0. A flowing through a Hall-Heroult cell for 1.00h?
13. Sea-water contains 1272 g of  $\text{Mg}^{2+}$  per metric ton (1 mega gram). How much of slaked lime must be added to 1.0 metric ton of sea water to precipitate all of the  $\text{Mg}^{2+}$  ion? ( $\text{Mg} = 24$ ,  $\text{Ca} = 40$ )

## Exercise 2

### (Stage 2 : High Skill Problem Solving)

#### Only One Option Correct

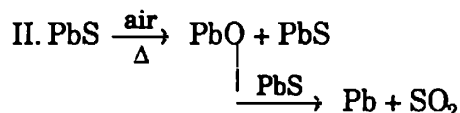
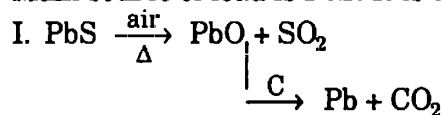
1. Si of high purity to be used in semiconductor can be prepared by following methods:



Better method is

- (a) I (b) II  
 (c) both (a) and (b) (d) None of these

2. Main source of lead is  $\text{PbS}$ . It is converted to Pb by:



Self-reduction process is

- (a) I (b) II  
 (c) both (a) and (b) (d) None of these

3. Match the compounds (A) with their applications/colour in (B)

| A                                                    | B                          |
|------------------------------------------------------|----------------------------|
| I. $\text{Pb}_3\text{O}_4$                           | W. white lead              |
| II. $(\text{PbCO}_3)_2 \cdot \text{Pb}(\text{OH})_2$ | X. rust proofing sheets    |
| III. $\text{Ca}_2\text{PbO}_4$                       | Y. road signs and markings |
| IV. $\text{PbCrO}_4$                                 | Z. red lead                |

Choose the correct alternate

| I     | II | III | I |
|-------|----|-----|---|
| (a) Y | Z  | X   | W |
| (b) X | W  | Y   | Z |
| (c) Z | W  | X   | Y |
| (d) X | Y  | W   | Z |

4.  $\text{P}_4\text{O}_{10}$  is converted to white phosphorus by

- (a) Al (b) C  
(c) Na (d) all are correct

5. Phosphine,  $\text{PH}_3$ , is prepared by

- (a)  $\text{Ca}_3\text{P}_2 + \text{H}_2\text{O} \longrightarrow$  (b)  $\text{P}_4 + \text{NaOH} \longrightarrow$   
(c) both are correct (d) None is correct

6. Formation of  $\text{Ni}(\text{CO})_4$  and subsequent its decomposition into Ni and CO (recycled) makes the basis of Mond's process



$T_1$  and  $T_2$  are

- (a)  $100^\circ\text{C}$ ,  $50^\circ\text{C}$  (b)  $50^\circ\text{C}$ ,  $100^\circ\text{C}$   
(c)  $50^\circ\text{C}$ ,  $230^\circ\text{C}$  (d)  $230^\circ\text{C}$ ,  $50^\circ\text{C}$

7. Oxides of the various metals are converted into metal by heating but not in

- (a)  $\text{Ag}_2\text{O}$  (b)  $\text{CuO}$   
(c)  $\text{HgO}$  (d) all are correct

8. Of the following reduction processes

- I.  $\text{Fe}_2\text{O}_3 + \text{C} \longrightarrow \text{Fe}$   
II.  $\text{ZnO} + \text{C} \longrightarrow \text{Zn}$   
III.  $\text{Ca}_3(\text{PO}_4)_2 + \text{C} \longrightarrow \text{P}$   
IV.  $\text{PbO} + \text{C} \longrightarrow \text{Pb}$

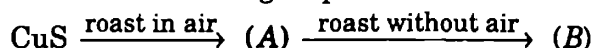
Correct processes are

- (a) all of these (b) all but III  
(c) all but IV (d) II and IV

9. Following reaction is not involved in *Thermite* process

- (a)  $3\text{Mn}_2\text{O}_4 + 8\text{Al} \longrightarrow 9\text{Mn} + 4\text{Al}_2\text{O}_3$   
(b)  $\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$   
(c)  $2\text{Fe} + \text{Al}_2\text{O}_3 \longrightarrow 2\text{Al} + \text{Fe}_2\text{O}_3$   
(d)  $\text{B}_2\text{O}_3 + 2\text{Al} \longrightarrow 2\text{B} + \text{Al}_2\text{O}_3$

10. Consider the following steps



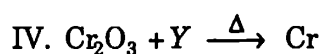
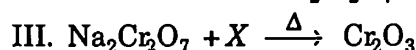
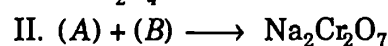
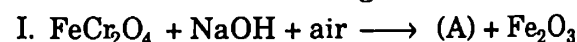
Which is not the correct statement?

- (a) It is self-reduction  
(b) It involves disproportionation  
 $\text{Cu}_2\text{S} \longrightarrow \text{Cu} + \text{CuS}$   
(c) (A) is a mixture of  $\text{CuO}$  and  $\text{CuS}$  and (B) is a mixture of  $\text{Cu}$  and  $\text{SO}_2$   
(d) All are incorrect statements

11. When  $\text{FeCr}_2\text{O}_4$  (chromite) is reduced with C in an electric-arc furnace

- (a) Cr and  $\text{Fe}_2\text{O}_3$  are formed  
(b) Fe and  $\text{Cr}_2\text{O}_3$  are formed  
(c) Fe and Cr (ferrochrome) are formed  
(d)  $\text{FeCrO}_4$  is formed

- $\text{FeCr}_2\text{O}_4$  (chromite) is a good source of Cr and its compounds like  $\text{Na}_2\text{CrO}_4$ ,  $\text{Na}_2\text{Cr}_2\text{O}_7$ . Questions 12 to 14 are based on following reactions:



12. Compounds (A) and (B) are

- (a)  $\text{Na}_2\text{CrO}_4$ ,  $\text{H}_2\text{SO}_4$   
(b)  $\text{Na}_2\text{Cr}_2\text{O}_7$ ,  $\text{HCl}$   
(c)  $\text{Na}_2\text{CrO}_5$ ,  $\text{H}_2\text{SO}_4$   
(d)  $\text{Na}_4[\text{Fe}(\text{OH})_6]$ ,  $\text{H}_2\text{SO}_4$

13. (X) and (Y) are

- (a) C and Al (b) Al and C  
(c) C in both (d) Al in both

14.  $\text{Na}_2\text{CrO}_4$  and  $\text{Fe}_2\text{O}_3$  are separated by dissolving in

- (a) conc.  $\text{H}_2\text{SO}_4$  (b)  $\text{NH}_3$   
(c)  $\text{H}_2\text{O}$  (d) dil.  $\text{HCl}$

15. Match the reactions taking place in blast furnace with temperature-range of operations:

| Reactions                                                                         | Temperature range         |
|-----------------------------------------------------------------------------------|---------------------------|
| (A) : $\text{Fe}_2\text{O}_3 + \text{CO} \longrightarrow \text{CO}_2 + \text{Fe}$ | (I) $1200^\circ\text{C}$  |
| (B) : $\text{C} + \text{CO}_2 \longrightarrow \text{CO}$                          | (II) $900^\circ\text{C}$  |
| (C) : $\text{C} + \text{H}_2\text{O} \longrightarrow \text{CO} + \text{H}_2$      | (III) $600^\circ\text{C}$ |
| (D) : $\text{CaO} + \text{SiO}_2 \longrightarrow \text{CaSiO}_3$                  | (IV) $1000^\circ\text{C}$ |

Choose the correct alternate

| A      | B   | C   | D   |
|--------|-----|-----|-----|
| (a) IV | III | II  | I   |
| (b) II | IV  | III | I   |
| (c) I  | II  | IV  | III |
| (d) I  | II  | III | IV  |

16. Match column (A) (process) with column (B) (electrolyte).

| A (process)                | B (electrolyte)                                                 |
|----------------------------|-----------------------------------------------------------------|
| (I) Downs cell             | (W) Fused $\text{MgCl}_2$                                       |
| (II) Dow sea water process | (X) Fused ( $\text{Al}_2\text{O}_3 + \text{Na}_3\text{AlF}_6$ ) |
| (III) Hall-Heroult         | (Y) Fused $\text{KHF}_2$                                        |
| (IV) Moissan               | (Z) Fused (40% $\text{NaCl}$ + 60% $\text{CaCl}_2$ )            |

Choose the correct alternate

| I     | II | III | IV | I     | II | III | IV |
|-------|----|-----|----|-------|----|-----|----|
| (a) Z | W  | X   | Y  | (b) X | Y  | Z   | W  |
| (c) W | Z  | X   | Y  | (d) X | Z  | W   | Y  |

17. In the Pidgeon process, Mg is produced by  
 (a) electrolysis of fused  $\text{MgCl}_2$   
 (b) reducing calcined dolomite with ferrosilicon at high temperature under pressure  
 (c) both (a) and (b)  
 (d) none of the above

18. Boron can be obtained by various methods but not by  
 (a) thermal decomposition of  $\text{B}_2\text{H}_6$   
 (b) pyrolysis of  $\text{BI}_3$  (van Arkel)  
 (c) reducing  $\text{BCl}_3$  with  $\text{H}_2$   
 (d) electrolysis of fused  $\text{BCl}_3$

19. Following method is not used for extraction of Al  
 (a) van Arkel (b) Serpeck  
 (c) Bayer (d) Hall-Heroult

20.  $\text{B}_4\text{C}$  (boron carbide) is used except  
 (a) to extract boron  
 (b) as an abrasive for polishing  
 (c) for making bullet-proof clothing  
 (d) for making diborane

21. In the extraction of nickel by Mond's process, the metal is obtained by  
 (a) electrochemical reduction  
 (b) thermal decomposition  
 (c) chemical reduction by aluminium  
 (d) reduction by carbon

22. Which one of the following statements is not correct?  
 (a) Nickel forms  $\text{Ni}(\text{CO})_4$   
 (b) All the transition metals form monometallic carbonyls  
 (c)  $\text{Ni}(\text{CO})_4$  is volatile and decomposes into Ni and CO  
 (d) Transition metals form complexes

23. Match List I with List II and select the correct answer using the codes given below the lists:

| List I            | List II      |
|-------------------|--------------|
| A. Carnallite     | 1. Zinc      |
| B. Calamine       | 2. Titanium  |
| C. Ilmenite       | 3. Magnesium |
| D. Chalcocopyrite | 4. Copper    |

| A     | B | C | D |
|-------|---|---|---|
| (a) 1 | 3 | 2 | 4 |
| (b) 1 | 3 | 4 | 2 |
| (c) 3 | 1 | 4 | 2 |
| (d) 3 | 1 | 2 | 4 |

24. Which of the following is not an ore?  
 (a) Malachite (b) Calamine  
 (c) Stellite (d) Cerussite

25. In the metallurgy of iron, when  $\text{CaCO}_3$  is added to blast furnace, calcium ion appears as  
 (a) CaO (b) metallic Ca  
 (c) gangue (d) slag

26. Iron obtained from blast furnace is  
 (a) wrought iron (b) cast iron  
 (c) pig iron (d) steel

27. Four metals and their methods of refinement are given:

- (i) Ni, Cu, Zr, Ga  
 (ii) Electrolysis, van Arkel process, Zone refining, Mond's process

Choose the right method for each:

- (a) Ni : Electrolysis, Cu : van Arkel process, Zr : Zone refining, Ga : Mond's process  
 (b) Ni : Mond's process, Cu : Electrolysis, Zr : van Arkel process, Ga : Zone refining  
 (c) Ni : Mond's process, Cu : van Arkel process, Zr : Zone refining, Ga : Electrolysis  
 (d) Ni : Electrolysis, Cu : Zone refining, Zr : van Arkel process, Ga : Mond's process

28. On igniting  $\text{Fe}_2\text{O}_3$  at  $1400^\circ\text{C}$ , the product obtained is  
 (a)  $\text{Fe}_2\text{O}_3$  melt (b) FeO  
 (c)  $\text{Fe}_3\text{O}_4$  (d) metallic iron

29. Consider the following metallurgical processes

- I. Heating impure metal with CO and distilling the resulting volatile carbonyl (b.p.  $43^\circ\text{C}$ ) and finally decomposing at  $150^\circ$  to  $200^\circ\text{C}$  to get the pure metal  
 II. Heating the sulphide ore in air until a part is converted to oxide and then further heating in the absence of air to let the oxide react with unchanged sulphide  
 3. Electrolysing the molten electrolyte containing approximately equal amounts of the metal chloride and  $\text{CaCl}_2$  to obtain the metal

The processes used for obtaining sodium, nickel and copper are respectively

- (a) I, II and III (b) II, III and I  
 (c) III, I and II (d) II, I and III

30. Extraction of aluminium from aluminium oxide ( $\text{Al}_2\text{O}_3$ ) is best done by  
 (a) electrolytic reduction of  $\text{Al}_2\text{O}_3$   
 (b) reduction of  $\text{Al}_2\text{O}_3$  with carbon  
 (c) reduction of  $\text{Al}_2\text{O}_3$  with sodium  
 (d) reduction of  $\text{Al}_2\text{O}_3$  with CO

31. Consider the following statements:

Roasting is carried out to

- I. convert sulphide to oxide and sulphate  
 II. remove water of hydration  
 III. melt the ore

4. remove arsenic and sulphur impurities

Of these statements

- (a) I, II and III are correct

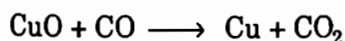
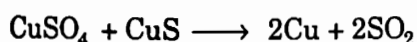
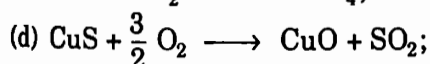
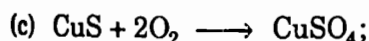
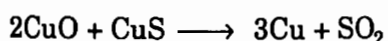
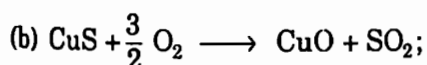
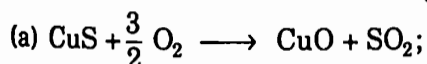


- (b) I and IV are correct  
(c) I, II and IV are correct  
(d) II, III and IV are correct
32. The element which could be extracted by electrolytic reduction of its oxide dissolved in a high temperature melt is  
(a) sodium (b) magnesium  
(c) fluorine (d) aluminium
33. Chemical leaching is useful in the concentration of  
(a) copper pyrites (b) bauxite  
(c) galena (d) cassiterite
34. Carbon cannot be used in the reduction of  $\text{Al}_2\text{O}_3$  because  
(a) it is an expensive proposition  
(b) the enthalpy of formation of  $\text{CO}_2$  is more than that of  $\text{Al}_2\text{O}_3$   
(c) pure carbon is not easily available  
(d) the enthalpy of formation of  $\text{Al}_2\text{O}_3$  is too high
35. In which of the following isolations no reducing agent is required?  
(a) Iron from haematite  
(b) Aluminium from bauxite  
(c) Mercury from cinnabar  
(d) Zinc from zinc blende
36. Which one of the following is not a method of concentration of metals?  
(a) Gravity separation  
(b) Froth flotation process  
(c) Electromagnetic separation  
(d) Smelting
37. Blister Cu is about  
(a) 60% Cu (b) 90% Cu  
(c) 98% Cu (d) 100% Cu
38. There are following extraction process of silver but not  
(a) as a side product in electrolytic refining of copper  
(b) Parke's process in which Zn is used to extract silver by solvent extraction from molten lead  
(c) by reaction of silver sulphide with KCN and then reaction of soluble complex with Zn.  
(d) by heating  $\text{Na}[\text{Ag}(\text{CN})_2]$
39.  $\text{Ag}_2\text{S} + \text{NaCN} \longrightarrow (\text{A})$   
 $(\text{A}) + \text{Zn} \longrightarrow (\text{B})$   
(B) is a metal. Hence, (A) and (B) are  
(a)  $\text{Na}_2[\text{Zn}(\text{CN})_4]$ , Zn (b)  $\text{Na}[\text{Ag}(\text{CN})_2]$ , Ag  
(c)  $\text{Na}_2[\text{Ag}(\text{CN})_4]$ , Ag (d)  $\text{Na}_3[\text{Ag}(\text{CN})_4]$ , Ag
40. Refining of silver is done by  
(a) liquation (b) Poling  
(c) cupellation (d) van Arkel method
41. Bessemerisation is carried out for  
I : Fe, II : Cu, III : Al, IV : silver  
(a) I, II (b) II, III  
(c) III, IV (d) I, III
42. Match the method of concentration of the ore in column I with the ore in column II and select the correct alternate:
- | Column I                | Column II                         |
|-------------------------|-----------------------------------|
| X : Magnetic separation | A : $\text{Ag}_2\text{S}$         |
| Y : Froth flotation     | B : $\text{FeCr}_2\text{O}_4$     |
| Z : Gravity separation  | C : $\text{Al}_2(\text{SiO}_3)_3$ |
- 
- | X     | Y | Z |
|-------|---|---|
| (a) A | B | C |
| (b) B | A | C |
| (c) C | A | B |
| (d) B | C | A |
43. Which of the following does not contain Mg?  
(a) Magnetite (b) Magnesite  
(c) Asbestos (d) Carnallite
44. Calcination is the process of heating the ore  
(a) in inert gas  
(b) in the presence of air  
(c) in the absence of air  
(d) in the presence of CaO and MgO
45.  $\text{Ag}_2\text{S} + \text{NaCN} + \text{Zn} \longrightarrow \text{Ag}$   
This method of extraction of Ag by complex formation and then its displacement is called  
(a) Parke's method  
(b) Mac Arthur-Forrest method  
(c) Serpeck method  
(d) Hall's method
46. The slag obtained during the extraction of copper from copper pyrites is composed of  
(a)  $\text{Cu}_2\text{S}$  (b)  $\text{CuSiO}_3$   
(c)  $\text{FeSiO}_3$  (d)  $\text{SiO}_2$
47. In zone-refining method the molten zone  
(a) consists of impurities only  
(b) contains more impurity than the original metal  
(c) contains the purified metal only  
(d) moves to either side
48. Reduction of a metal oxide by excess carbon at high temperature is a method for the commercial preparation of some metals. This method can be successfully applied in the case of  
(a) BeO and  $\text{Al}_2\text{O}_3$  (b) ZnO and  $\text{Fe}_2\text{O}_3$   
(c) CaO and  $\text{Cr}_2\text{O}_3$  (d) BaO and  $\text{U}_3\text{O}_8$
49. Match List I with List II and select the correct answer using the codes gives below the lists :
- | List I              | List II                                    |
|---------------------|--------------------------------------------|
| A. van Arkel method | 1. Manufacture of caustic soda             |
| B. Solvay process   | 2. Purification of titanium                |
| C. Cupellation      | 3. Manufacture of $\text{Na}_2\text{CO}_3$ |
| D. Poling           | 4. Purification of copper                  |
|                     | 5. Refining of silver                      |

Codes

|     | A | B | C | D |
|-----|---|---|---|---|
| (a) | 2 | 1 | 3 | 4 |
| (b) | 4 | 3 | 2 | 5 |
| (c) | 2 | 3 | 5 | 4 |
| (d) | 5 | 1 | 3 | 4 |

50. Formation of metallic copper from the sulphide ore in the normal thermo-metallurgical process essentially involves which one of the following reaction?



51. Annealing of steel is the process of heating steel

- (a) to a bright red hot and then cooling it slowly
- (b) to a bright red hot and then cooling it suddenly
- (c) to a temperature much below redness and cooling it slowly
- (d) none of the above

52. Out of  $\text{Cu}_2\text{S}$ ,  $\text{HgS}$ ,  $\text{Ag}_2\text{S}$  and  $\text{ZnS}$ , roasting will convert the minerals into metal in case of

- (a)  $\text{Cu}_2\text{S}$ ,  $\text{ZnS}$
- (b)  $\text{HgS}$ ,  $\text{ZnS}$
- (c)  $\text{Cu}_2\text{S}$ ,  $\text{Ag}_2\text{S}$
- (d)  $\text{HgS}$

53. The method of zone refining of metals is based on the principle of

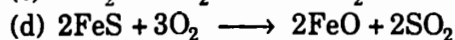
- (a) greater noble character of the solid metal than that of the impurity
- (b) greater solubility of the impurity in the molten state than in the solid
- (c) greater mobility of the pure metal than that of impurity
- (d) higher melting point of the impurity than that of the pure metal

54. Splitting of silver is

- (a) reduction of ammoniacal silver nitrate solution by tartarate
- (b) extraction of silver from its ore  $\text{Ag}_2\text{S}$ , by hydrometallurgy
- (c) making of silver amalgam during filling of teeth
- (d) cooling of molten silver with the evolution of oxygen causing violent spurting

55. In the extraction of Cu, the reaction takes place in bessemer converter is

- (a)  $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2$
- (b)  $2\text{CuFeS}_2 + \text{O}_2 \longrightarrow \text{Cu}_2\text{S} + \text{FeS} + \text{SO}_2$



56. Sodium is made by the electrolysis of molten mixture of about 40%  $\text{NaCl}$  and 60%  $\text{CaCl}_2$  because

- (a)  $\text{CaCl}_2$  helps in conduction of electricity
- (b)  $\text{Ca}^{2+}$  can reduce  $\text{NaCl}$  to  $\text{Na}$
- (c)  $\text{Ca}^{2+}$  can displace  $\text{Na}$  from  $\text{NaCl}$
- (d) this mixture has a lower melting point than  $\text{NaCl}$

57. Calcium is obtained by the

- (a) roasting of limestone
- (b) electrolysis of solution of calcium chloride in  $\text{H}_2\text{O}$
- (c) electrolysis of molten anhydrous calcium chloride
- (d) reduction of calcium chloride with carbon

58. Which one of the following elements constitutes a major impurity in pig iron?

- (a) Silicon
- (b) Oxygen
- (c) Sulphur
- (d) Graphite

59. Purification of aluminium by electrolytic refining, is known as

- (a) Hall's process
- (b) Baeyer's process
- (c) Hoope's process
- (d) Serpeck's process

60. Cassiterite is an ore of

- (a) Mn
- (b) Ni
- (c) Sb
- (d) Sn

61. The process used for purification  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  is

- (a) magnetic separation
- (b) froth flotation
- (c) leaching
- (d) liquation

62. Froth flotation is a process of

- (a) oxidation
- (b) reduction
- (c) refining
- (d) concentration

63. Malachite is an ore of

- (a) silver
- (b) mercury
- (c) magnesium
- (d) copper

64. Flux is used to remove

- (a) basic impurities
- (b) acidic impurities
- (c) all types of impurities
- (d) acidic and basic both impurities

65. Mac Arthur process is used for the extraction of

- (a) Al
- (b) Ag
- (c) Cu
- (d) Zn

66. The chemical process in the production of steel from haematite ore involves

- (a) reduction
- (b) oxidation
- (c) reduction followed by oxidation
- (d) oxidation followed by reduction

67. Electrolytic reduction of alumina to aluminium by Hall-Heroult process is carried out

- (a) in the presence of  $\text{NaCl}$
- (b) in the presence of fluorite

- (c) in the presence of cryolite which forms a melt with lower melting temperature  
 (d) in the presence of cryolite which forms a melt with higher melting temperature
68. Which of the following ore is concentrated by both, magnetic and gravimetric separation?  
 (a) Dolomite (b) Tinstone  
 (c) Galena (d) Bauxite
69. Which of the following processes is used in extractive metallurgy of magnesium?  
 (a) Fused salt electrolysis  
 (b) Self reduction  
 (c) Aqueous solution electrolysis  
 (d) Thermite reduction
70. In the process of extraction of gold,  

$$\text{Roasted gold ore} + \text{CN}^- + \text{H}_2\text{O} \xrightarrow{\text{O}_2} [\text{X}] + \text{OH}^-$$

$$[\text{X}] + \text{Zn} \longrightarrow [\text{Y}] + \text{Au}$$
 Identify the complexes [X] and [Y].  
 (a)  $\text{X} = [\text{Au}(\text{CN})_2]^-$ ,  $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$   
 (b)  $\text{X} = [\text{Au}(\text{CN})_4]^{3-}$ ,  $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$   
 (c)  $\text{X} = [\text{Au}(\text{CN})_2]^-$ ,  $\text{Y} = [\text{Zn}(\text{CN})_6]^{4-}$   
 (d)  $\text{X} = [\text{Au}(\text{CN})_4]^-$ ,  $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$
71. The methods chiefly used for the extraction of lead and tin from their ores are respectively  
 (a) self reduction and carbon reduction  
 (b) self reduction and electrolytic reduction  
 (c) carbon reduction and self reduction  
 (d) cyanide process and carbon reduction
72. Extraction of zinc from zinc blende is achieved by  
 (a) electrolytic reduction  
 (b) roasting followed by reduction with carbon  
 (c) roasting followed by reduction with another metal  
 (d) roasting followed by self-reduction
73. Which one of the following statements is correct? In the metallurgy of sodium by electrolysis, excess of calcium chloride is mixed with sodium chloride to  
 (a) make the latter a good conductor  
 (b) make the latter soft  
 (c) generate more energy for the electrolytic cell  
 (d) assist liquefaction of the latter at a much lower temperature
74. Consider the following statements  
 I : Pig iron is malleable and ductile.  
 II : Pig iron can be melted to produce cast iron of desired shapes.  
 III : Wrought iron is obtained by heating pig iron with iron oxide in a furnace.  
 Which of the statement(s) given above is/are correct?  
 (a) I only (b) I and II  
 (c) II and III (d) III only
75. Main process for extracting nickel in the pure form uses which one of the following?  
 (a) Vapour phase refining  
 (b) Zone refining  
 (c) Electrolysis  
 (d) Solvent extraction
76. Which represents correct matching of metals with their minerals?
- | Mg            | Na        | Cu       | Al        |
|---------------|-----------|----------|-----------|
| (a) chloride  | chloride  | sulphide | silicate  |
| (b) carbonate | chloride  | sulphide | oxide     |
| (c) carbonate | carbonate | oxide    | phosphate |
| (d) oxide     | chloride  | sulphide | oxide     |
77. Which of the following metals are found in native state?  
 Ag, Pt, C, Si, N, O, Mg, Na, Pb.  
 (a) Ag, Pt, C, N, O (b) Ag, Pt, Mg  
 (c) Ag, Pt, Pb, Mg (d) Ag, Pt
78. Most abundant metal in earth crust is  
 (a) Al (b) O  
 (c) Fe (d) Si
79. Followed by oxygen which element is the most abundant in human body  
 (a) C (b) H  
 (c) Ca (d) P
80. Select correct statement.  
 (a) Based on reactivity series, occurrence of certain elements takes place in native state  
 (b) Due to basic nature of oxides of alkaline earth elements, they combine with atmospheric acidic oxides giving salts  
 (c) Both (a) and (b) are correct  
 (d) None of the above is correct
81. Which is not the correct statement?  
 (a) Cassiterite, chromite and pitchblende are concentrated by hydraulic washing (Tabling).  
 (b) Pure  $\text{Al}_2\text{O}_3$  is obtained from the bauxite ore by leaching in the Baeyer's process.  
 (c) Sulphide ore is concentrated by calcination method.  
 (d) Roasting can convert sulphide into oxide or sulphate and part of sulphide may also act as a reducing agent.
82. NaCN is sometimes added in the froth flotation process as a depressant when ZnS and PbS minerals are expected because  
 (a)  $\text{Pb}(\text{CN})_2$  is precipitated while no effect as ZnS  
 (b) ZnS forms soluble complex  $\text{Na}_2[\text{Zn}(\text{CN})_4]$  while PbS forms froth  
 (c) PbS forms soluble complex  $\text{Na}_2[\text{Pb}(\text{CN})_4]$  while ZnS forms froth  
 (d) NaCN is never added in froth flotation process

83. Which method is not correct given for refining of crude metals?
- Distillation : zinc and mercury
  - Liquation : tin
  - van Arkel : Zirconium
  - Mond process : lead
84. Self-reduction of CuS to Cu can be carried out in:
- Bessemer converter
  - Pierce-Smith converter
  - both (a) and (b)
  - None of these
85. Select incorrect reduction process
- $2[\text{Ag}(\text{CN})_2]^- + \text{Zn} \longrightarrow [\text{Zn}(\text{CN})_4]^{2-} + 2\text{Ag}$
  - $\text{CuO} + \text{H}_2 \longrightarrow \text{Cu} + \text{H}_2\text{O}$
  - $\text{ZnO} + \text{H}_2 \longrightarrow \text{Zn} + \text{H}_2\text{O}$
  - $\text{MgO} + \text{C} \longrightarrow \text{Mg} + \text{CO}$
86. Ellingham diagram represents
- change of  $\Delta G$  with temperature
  - change of  $\Delta H$  with temperature
  - change of  $\Delta G$  with pressure
  - change of  $(\Delta G - T\Delta S)$  with temperature
87. Selection of temperature to carry out a reduction process depends so as to make
- $\Delta G$  negative
  - $\Delta G$  positive
  - $\Delta H$  negative
  - $\Delta H$  positive
88. The reduction of an oxide by aluminium is called
- Ellingham process
  - Goldschmidt's aluminothermite process
  - Kroll's process
  - van Arkel process
89. Select correct statement.
- In the decomposition of an oxide, into oxygen and gaseous metal, entropy increases.
  - Decomposition of an oxide is an endothermic change.
  - To make  $\Delta G^\circ$  negative, temperature should be high enough so that  $T \Delta S^\circ > \Delta H^\circ$ .
  - All of the above are correct statements
90. Which does not represent correct method?
- $\text{TiCl}_2 + 2\text{Mg} \longrightarrow \text{Ti} + 2\text{MgCl}_2$  : Kroll
  - $\text{Ni}(\text{CO})_4 \longrightarrow \text{Ni} + 4\text{CO}$  : Mond
  - $\text{Ag}_2\text{CO}_3 \longrightarrow 2\text{Ag} + \text{CO}_2 + \frac{1}{2}\text{O}_2$  : van Arkel
  - $\text{ZrI}_4 \longrightarrow \text{Zr} + 2\text{I}_2$  : van Arkel
91. Pyrometallurgical method used for the extraction of copper from sulphide ore
- is a dry method
  - involves concentration by leaching the sulphide ore with dil.  $\text{H}_2\text{SO}_4$
  - involves concentration of the sulphide ore by froth flotation process
  - statement given in (b) is incorrect
92. Blister copper is
- impure copper
  - obtained in self-reduction process during bessemerisation
  - both (a) and (b) are correct
  - none of the above is correct
93. Froth flotation process used for the concentration of sulphide ore
- is based on the difference in wettability of different minerals
  - uses sodium ethyl xanthate,  $\text{C}_2\text{H}_5\text{OCS}_2\text{Na}$  as collector
  - uses NaCN as depressant in the mixture of ZnS and PbS when ZnS forms soluble complex and PbS forms froth
  - all of the above are correct
94. Select correct statement(s) about differentiation flotation
- is used to concentrate mixture of sulphides at different stages
  - zinc sulphate is used to depress zinc sulphide and PbS forms froth
  - copper sulphate is used to activate depressed lead sulphide and  $\text{O}_2$  is blown to make froth
  - all of the above are correct statements
95. Which step is not involved in hydrometallurgical process?
- $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \longrightarrow 6\text{Cu} + \text{SO}_2$
  - $\text{CuFeS}_2 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{FeSO}_4 + 2\text{H}_2\text{S}$
  - $\text{CuSO}_4 + \text{Fe} \longrightarrow \text{FeSO}_4 + \text{Cu}$
  - $\text{CuCO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{H}_2\text{O} + \text{CO}_2$
96. When alloy of silver and lead is rich in silver,
- cupellation process is used
  - Parke's method is used
  - Pattinson's method is used
  - any of the above methods can be used
97. Magistral is the burnt pyrites containing
- sulphates of iron and copper
  - sulphates and oxides of iron and copper
  - oxides of iron and copper
  - sulphides of silver and lead
98. In the leaching of  $\text{Ag}_2\text{S}$  with NaCN, a stream of air is also passed. It is because of
- reversible nature of reaction between  $\text{Ag}_2\text{S}$  and NaCN
  - to oxide  $\text{Na}_2\text{S}$  formed into  $\text{Na}_2\text{S}_2\text{O}_3$  and sulphur
  - both (a) and (b)
  - none of the above
99.  $(\text{Ag} + \text{Pb})$  alloy  $\xrightarrow[\text{is added}]{\text{melt and zinc}}$   $(\text{Ag} + \text{Pb} + \text{Zn})$  melt  $\xrightarrow{\text{cool}}$ 

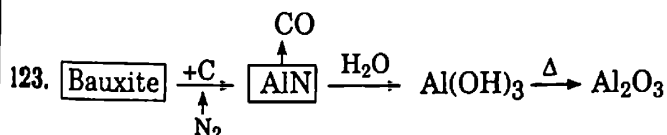
|         |
|---------|
| Layer X |
| Layer Y |
- Select correct statement(s) based on above scheme
- layer X contains zinc and silver
  - layer Y contains lead and silver but amount of silver in this layer is smaller than in the layer X.
  - X and Y are immiscible layers
  - all of the above are correct statement

100.  $\text{AgCl} + \text{Na}_2\text{CO}_3 \longrightarrow \text{Ag}_2\text{CO}_3 \xrightarrow{\Delta} X$ ,  $X$  is  
 (a)  $\text{Ag}_2\text{O}$  and  $\text{CO}_2$  (b)  $\text{Ag}$ ,  $\text{O}_2$  and  $\text{CO}_2$   
 (c)  $\text{Ag}_2\text{O}_2$  and  $\text{CO}_2$  (d) no effect
101. Purest form of iron is  
 (a) cast iron (b) wrought iron  
 (c) pig iron (d) none of these
102. The most important method of making steel is  
 (a) BOP process (b) BOD process  
 (c) puddling process (d) smelting
103. Cementite is  
 (a) predominant content of cement  
 (b) a mineral of calcium  
 (c) a carbide of iron in steel  
 (d) none of the above
104. Phosphorus separates, in the extraction of iron, as  
 (a) slag,  $\text{Ca}_3(\text{PO}_4)_2$  (b) volatile,  $\text{P}_2\text{O}_5$   
 (c) slag,  $\text{Mg}_3(\text{PO}_4)_2$  (d)  $\text{Ca}_3\text{P}_2$
105. Tempering of steel  
 (a) is the heating the steel to appropriate temperature and then cooling it rapidly  
 (b) increases mechanical strength  
 (c) changes ratio of carbon in cementite  
 (d) all of the above
106. Mg can be obtained  
 (a) by heating  $\text{MgCl}_2$  (anhydrous) with Na in the atmosphere of coal gas  
 (b) by electrolysis of fused carnallite  
 (c) by both the methods  
 (d) by none of the above methods
107. During the electrolysis of carnallite,  $\text{MgCl}_2$  is decomposed and not KCl. This is because of  
 (a) lower decomposition voltage of  $\text{MgCl}_2$  than that of KCl  
 (b) reverse reaction  $\text{MgCl}_2 + 2\text{K} \longrightarrow \text{Mg} + 2\text{KCl}$  if KCl is decomposed under other experimental condition  
 (c) both (a) and (b)  
 (d) none of the above
108. NaCl and  $\text{CaCl}_2$  are also added to fused  $\text{MgCl}_2$  in the electrolysis of  $\text{MgCl}_2$  since  
 (a) melting point is decreased and conductivity is increased  
 (b) melting point is increased and conductivity is decreased  
 (c) melting point and conductivity both are decreased  
 (d) melting point and conductivity both are increased
109. Which is the sulphate ore of Mg?  
 (a) Dolomite (b) Carnallite  
 (c) Magnesite (d) Kieserite
110. Which is the chloride ore of Mg?  
 (a) Kieserite (b) Carnallite  
 (c) Epsomite (d) Dolomite
111. Black tin is  
 (a) an alloy of Sn (b) an allotrope of Sn  
 (c) 60–70 per cent  $\text{SnO}_2$  (d) 100 per cent  $\text{SnO}_2$
112.  $\text{SnO}_2$  is reduced to metallic Sn on smelting oxide with anthracite, limestone and sand. In this, function of sand is  
 (a) it acts as a flux  
 (b) it removes basic impurities as slag  
 (c) both as in (a) and (b)  
 (d) none of the above
113. Poling process  
 (a) reduced  $\text{SnO}_2$  to Sn  
 (b) oxidises impurities like iron and removes as scum  
 (c) uses green poles  
 (d) involves all of the above
114. Refining of tin cannot be done by  
 (a) cupellation (b) liquation  
 (c) poling (d) electrorefining
115. Which is not the correct process-mineral matching in metallurgical extraction?  
 (a) Leaching : Ag  
 (b) Zone-refining : Sn  
 (c) Liquation : Sn  
 (d) van Arkel : Zr
116. Softening of lead means:  
 (a) melting pure lead at high temperature  
 (b) removal of impurities, except silver, present in commercial lead  
 (c) formation of lead alloy  
 (d) formation of 100% pure lead
117. Softened lead is desilverised by  
 (a) Parke's method (b) Pattinson's method  
 (c) both (a) and (b) (d) none of these
118. Self reduction of the sulphide ore takes place during  
 (a) roasting (b) smelting  
 (c) calcination (d) cupellation
119. Lead pencil contains  
 (a) graphite (b) softened lead  
 (c) galena (d) anglesite
120. Select incorrect statement.  
 (a) When the lead-silver alloy is rich in silver, lead is removed by the cupellation process  
 (b) When the lead-silver alloy is rich in lead, lead is removed by Parke's or Pattinson's process  
 (c) Zinc forms an alloy with lead from which lead is separated  
 (d) Zinc forms an alloy with silver, from which zinc is separated by distillation
121. In the Baeyer's process:  
 (a)  $\text{Al}_2\text{O}_3$  goes into solution as soluble  $\text{Al}(\text{OH})_4^-$  while other basic oxides as  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  remain insoluble.

- (b)  $\text{Al}_2\text{O}_3$  changes to  $\text{AlN}$  which in turn decomposed by  $\text{H}_2\text{O}$   
 (c)  $\text{Al}_2\text{O}_3$  changes to  $\text{Al}_2(\text{CO}_3)_3$  which changes to  $\text{AlCl}_3$   
 (d) none of the above is correct

122. In electrolysis of  $\text{Al}_2\text{O}_3$  by Hall-Heroult process

- (a) Cryolite  $\text{Na}_3[\text{AlF}_6]$  lowers the m.p. of  $\text{Al}_2\text{O}_3$  and increases its electrical conductivity.  
 (b) Al is obtained at cathode and probably  $\text{CO}_2$  at anode  
 (c) both (a) and (b) are correct  
 (d) none of the above is correct



This flow-sheet is for

- (a) Baeyer's process (b) Serpeck's process  
 (c) Hall's process (d) Kroll's process

124. Corundum is ..... mineral of Al.

- (a) silicate (b) oxide  
 (c) double salt (d) sulphate

125. Which mineral has been named incorrectly?

- (a) Bauxite :  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$   
 (b) Corundum :  $\text{Al}_2\text{O}_3$   
 (c) Cryolite :  $3\text{NaF} \cdot \text{AlF}_3$   
 (d) Feldspar :  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$

126. The chemical process in the production of steel from haematite ore involves

- (a) reduction  
 (b) oxidation  
 (c) reduction followed by oxidation  
 (d) oxidation followed by reduction

127. Electrolytic reduction of alumina to aluminium by Half-Heroult process is carried out

- (a) in the presence of  $\text{NaCl}$   
 (b) in the presence of fluorite  
 (c) in the presence of cryolite which forms a melt with lower melting temperature  
 (d) in the presence of cryolite which forms a melt with higher melting temperature

128. The chemical composition of 'slag' formed during the smelting process in the extraction of copper is

- (a)  $\text{Cu}_2\text{O} + \text{FeS}$  (b)  $\text{FeSiO}_3$   
 (c)  $\text{CuFeS}_2$  (d)  $\text{Cu}_2\text{S} + \text{FeO}$

129. Which of the following processes is used in extractive metallurgy of magnesium?

- (a) Fused salt electrolysis  
 (b) Self reduction  
 (c) Aqueous solution electrolysis  
 (d) Thermite reduction

130. Calamine is

- (a)  $\text{ZnS}$  (b)  $\text{PbCO}_3$   
 (c)  $\text{ZnCO}_3$  (d)  $\text{MgCO}_3$

131. The methods chiefly used for the extraction of lead and tin from their ores are respectively

- (a) self reduction and carbon reduction  
 (b) self reduction and electrolytic reduction  
 (c) carbon reduction and self reduction  
 (d) cyanide process and carbon reduction

132. Which ore contains both iron and copper?

- (a) Cuprite (b) Chalcocite  
 (c) Chalcopyrite (d) Malachite

133. Extraction of zinc from zinc blende is achieved by

- (a) electrolytic reduction  
 (b) roasting followed by reduction with carbon  
 (c) roasting followed by reduction with another metal  
 (d) roasting followed by self-reduction

134. The method of zone refining of metals is based on the principle of

- (a) greater noble character of the solid metal than that of the impurity  
 (b) greater solubility of the impurity in the molten state than in the solid  
 (c) greater mobility of the pure metal than that of impurity  
 (d) higher melting point of the impurity than that of the pure metal

135.  $\text{Al}_2\text{O}_3$  can be converted to anhydrous  $\text{AlCl}_3$  by heating

- (a)  $\text{Al}_2\text{O}_3$  with  $\text{HCl}$  gas  
 (b)  $\text{Al}_2\text{O}_3$  with  $\text{NaCl}$  in solid state  
 (c) a mixture of  $\text{Al}_2\text{O}_3$  and carbon in dry  $\text{Cl}_2$  gas  
 (d)  $\text{Al}_2\text{O}_3$  with  $\text{Cl}_2$  gas

136. Flux is used to remove

- (a) silica (b) metal oxide  
 (c) silica and metal oxide (d) impurities from ore

137. The process of heating and suddenly cooling of steel is known as

- (a) tempering (b) annealing  
 (c) hardening (d) quenching

138. The metal which cannot be extracted by smelting process

- (a) Zn (b) Al  
 (c) Pb (d) Fe

139. Which of the following processes is related with the removal of sulphur by heating in the air?

- (a) Smelting (b) Calcination  
 (c) Annealing (d) Roasting

140. In electrorefining of copper, some gold is deposited as

- (a) cathode (b) electrode  
 (c) cathode mud (d) anode mud

141. Bessemer converter is used for preparation of  
 (a) steel (b) wrought iron  
 (c) pig iron (d) cast iron
142. Colemanite is  
 (a)  $\text{Ca}[\text{B}_3\text{O}_4(\text{OH}_2)] \cdot 2\text{H}_2\text{O}$   
 (b)  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$   
 (c)  $\text{Ca}(\text{OH})_2$   
 (d)  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 2\text{H}_2\text{O}$
143. Mac Arthur process is used for the extraction of  
 (a) Au (b) Ag  
 (c) Cu (d) Zn
144. Which of the following is not an iron ore?  
 (a) Caniterite (b) Magnetite  
 (c) Limonite (d) Copper pyrite
145. Thermite is a mixture of iron oxide and  
 (a) aluminium powder (b) zinc powder  
 (c) potassium metal (d) sodium metal
146. In the extraction of copper from its sulphide ore, the metal is formed by reduction of  $\text{Cu}_2\text{O}$  with  
 (a) FeS (b) CO  
 (c)  $\text{Cu}_2\text{S}$  (d)  $\text{SO}_2$
147. Which of the following is a carbonate ore?  
 (a) Pyrolusite (b) Malachite  
 (c) Diaspore (d) Cassiterite
148. Purification of alumina takes place by  
 (a) Bosch process (b) Hall's process  
 (c) Hoope's process (d) Quartation process
149. The hardest naturally occurring substance is  
 (a) iron (b) graphite  
 (c) diamond (d) astatine
150. Wolframite ore is separated from tinstone ore by the process of  
 (a) roasting (b) electromagnetic  
 (c) smelting (d) calcination
151. By annealing, steel  
 (a) becomes soft  
 (b) becomes liquid  
 (c) becomes hard and brittle  
 (d) is covered with a thin film of  $\text{Fe}_3\text{O}_4$
152. The process of purification of metals is represented by the following scheme  

$$\text{Ti} + 2\text{I}_2 \xrightarrow{250^\circ\text{C}} \text{TiI}_4 \xrightarrow{1400^\circ\text{C}} \text{Ti}_{\text{pure}} + \text{I}_2$$
  
 (a) cupellation (b) poling  
 (c) electrolytic refining (d) van-Arkel method
153. Among the following statements, the correct one is  
 (a) zinc blende and iron pyrites are sulphides  
 (b) calamine and siderite are carbonates  
 (c) malachite and chalcocite are the copper ore  
 (d) argentite and cuprite are oxides
154. The silver is extracted by Parke's process. The basis of this method is  
 (a) silver is immiscible in molten Zn  
 (b) Ag is miscible in NaCN  
 (c) Ag is more miscible in molten zinc than in molten Pb  
 (d) Ag is more miscible in molten Pb in comparison to molten zinc
155. Railway wagon axles are made by heating iron rods embedded in charcoal powder. This process is known as  
 (a) tempering (b) annealing  
 (c) sherar dishing (d) case hardening
156. Electric refining is used for refining of  
 (a) Cu (b) Fe  
 (c) Pb (d) Al
157. To dissolve argentite ore which of the following is used  
 (a)  $\text{Na}[\text{Ag}(\text{CN})_2]$  (b) NaCN  
 (c) NaCl (d) HCl
158. In aluminothermic process, Al acts as a  
 (a) flux (b) oxidising agent  
 (c) reducing agent (d) solder
159. Which of the following is not an ore of magnesium?  
 (a) Carnallite (b) Magnesium  
 (c) Dolomite (d) Gypsum
160. The formula of malachite ore is  
 (a)  $\text{Fe}_3\text{O}_4$  (b)  $\text{Mn}_3\text{O}_4$   
 (c) NiAs (d)  $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$
161. Which of the following has maximum percentage of copper?  
 (a)  $\text{Cu}_2\text{S}$  (b)  $\text{Cu}_2\text{O}$   
 (c)  $\text{CuFeS}_2$  (d)  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
162. The chief impurity present in red bauxite is  
 (a)  $\text{SiO}_2$  (b)  $\text{Fe}_2\text{O}_3$   
 (c)  $\text{K}_2\text{SO}_4$  (d) NaF
163. The extraction of which of the following metals involves bessemerisation?  
 (a) Fe (b) Ag  
 (c) Al (d) Cu
164. Which of the following metal is correctly matched with its ore?
- |     | Metal     | Ore         |
|-----|-----------|-------------|
| (a) | Zinc      | Calamine    |
| (b) | Silver    | Illmenite   |
| (c) | Magnesium | Cassiterite |
| (d) | Tin       | Azurite     |
165. A cuprous ore among the following is  
 (a) cuprite (b) malachite  
 (c) chalcopyrites (d) azurite

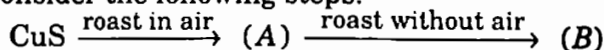
166. Aluminium oxide is not reduced by chemical reactions since  
 (a) reducing agent contaminates  
 (b) the process pollutes the environment  
 (c) aluminium oxide is highly stable  
 (d) aluminium oxide is reactive
167. Identify the reaction that does not take place during smelting process of copper extraction  
 (a)  $2\text{FeS} + 3\text{O}_2 \longrightarrow 2\text{FeO} + 2\text{SO}_2$   
 (b)  $\text{Cu}_2\text{O} + \text{FeS} \longrightarrow \text{Cu}_2\text{S} + \text{FeO}$   
 (c)  $2\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$   
 (d)  $\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3$
168. Gold is extracted by hydrometallurgical process, based on its property  
 (a) of being electropositive  
 (b) of being less reactive  
 (c) to form complexes which are water soluble  
 (d) to form salts which are water soluble
169. In blast furnace, iron oxide is reduced by  
 (a) hot blast of air (b) carbon monoxide  
 (c) carbon (d) silica
170. During the extraction of Fe the slag obtained is  
 (a)  $\text{FeSiO}_3$  (b)  $\text{FeO}$   
 (c)  $\text{CaSiO}_3$  (d)  $\text{MgSiO}_3$
171. The final step for the extraction of copper from copper pyrites in Bessemer converter involves the reaction  
 (a)  $\text{Cu}_2\text{S} + 2\text{FeO} \longrightarrow 2\text{Cu} + 2\text{Fe} + \text{SO}_2$   
 (b)  $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \longrightarrow 6\text{Cu} + \text{SO}_2$   
 (c)  $4\text{Cu}_2\text{O} + \text{FeS} \longrightarrow 8\text{Cu} + 2\text{FeSO}_4$   
 (d)  $2\text{Cu}_2\text{O} + \text{FeS} \longrightarrow 4\text{Cu} + \text{Fe} + \text{SO}_2$
172. Lead as impurity in the extraction of silver is removed by which process?  
 (a) Cyanide process  
 (b) Solvay process  
 (c) Parke's process  
 (d) Froth flotation process
173. The ore of aluminium is  
 (a) carnallite (b) malachite  
 (c) galena (d) bauxite
174. The process of zinc plating on iron sheet is known as  
 (a) annealing (b) roasting  
 (c) galvanization (d) smelting
175. A metal used to recover copper from a solution of  $\text{CuSO}_4$  is  
 (a) Fe (b) Hg  
 (c) Na (d) Ag
176. Gravity separation process is used for the concentration of  
 (a) calamine (b) haematite  
 (c) chalcopyrites (d) bauxite
177. In Mac-Arthur Forrest method, silver is extracted from solution of  $\text{Na}[\text{Ag}(\text{CN})_2]$  by the use of  
 (a) Fe (b) Mg  
 (c) Cu (d) Zn
178. Which of the following process is not involved in manufacturing of steel?  
 (a) Bessemer process (b) Open hearth process  
 (c) BOP (d) Thermite process
179. Bauxite is concentrated by  
 (a) chemical method  
 (b) roasting  
 (c) magnetic separation  
 (d) froth flotation process
180. The ore carnallite is represented by structure  
 (a)  $\text{Na}_2\text{Al}_2\text{O}_3$  (b)  $\text{Na}_3\text{AlF}_6$   
 (c)  $\text{KClMgCl}_2 \cdot 6\text{H}_2\text{O}$  (d)  $\text{Fe}_3\text{O}_4$
181. Which of the following statement is incorrect?  
 (a) Pure aluminium oxide is obtained by heating aluminium hydroxide.  
 (b) Cryolite lowers down the melting point of bauxite in electrolytic cell for extraction of aluminium.  
 (c) Carbonate ores are converted into oxides by roasting ore in air.  
 (d) Mercury cannot be produced by roasting the cinnabar ore in air.
182. A carbonate ore is  
 (a) carnallite (b) limonite  
 (c) siderite (d) horn silver
183. Chalcopyrites is an ore of  
 (a) gallium (b) copper  
 (c) calcium (d) magnesium
184. Thomas slag is  
 (a)  $\text{Ca}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  (b)  $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaSiO}_3$   
 (c)  $\text{MgSiO}_3$  (d)  $\text{CaSiO}_3$
185. Flux in the smelting process is added to  
 (a) decrease the solubility of impurities  
 (b) increase the fusion temperature of roasted ore  
 (c) convert impurities into slag  
 (d) all of the above

### One or More Than One Options Correct

1. Of the following reduction processes, correct processes are:  
 (a)  $\text{Fe}_2\text{O}_3 + \text{C} \longrightarrow \text{Fe}$   
 (b)  $\text{ZnO} + \text{C} \longrightarrow \text{Zn}$   
 (c)  $\text{Ca}_3(\text{PO}_4)_2 + \text{C} \longrightarrow \text{P}$   
 (d)  $\text{PbO} + \text{C} \longrightarrow \text{Pb}$
2. Following reaction(s) is/are not involved in Thermite process  
 (a)  $3\text{Mn}_2\text{O}_4 + 8\text{Al} \longrightarrow 9\text{Mn} + 4\text{Al}_2\text{O}_3$   
 (b)  $\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$   
 (c)  $2\text{Fe} + \text{Al}_2\text{O}_3 \longrightarrow 2\text{Al} + \text{Fe}_2\text{O}_3$   
 (d)  $\text{B}_2\text{O}_3 + 2\text{Al} \longrightarrow 2\text{B} + \text{Al}_2\text{O}_3$



3. Consider the following steps:



Which are the correct statements?

- (a) It is self-reduction
- (b) It involves disproportionation  

$$\text{Cu}_2\text{S} \longrightarrow \text{Cu} + \text{CuS}$$
- (c) (A) is a mixture of CuO and CuS and (B) is a mixture of Cu and SO<sub>2</sub>
- (d) (A) is a mixture of Cu and SO<sub>2</sub> and (B) is CuSO<sub>4</sub>

4. Phosphine is obtained by

- (a)  $\text{Ca}_3\text{P}_2 + \text{H}_2\text{O} \longrightarrow$
- (b)  $\text{P}_4 + \text{NaOH} \longrightarrow$
- (c)  $\text{CHCl}_3 + \text{O}_2 \longrightarrow$
- (d)  $\text{CCl}_4 + \text{O}_2 \longrightarrow$

5. Carbon cannot be used in the reduction of Al<sub>2</sub>O<sub>3</sub> because

- (a) It is an expensive proposition
- (b) The enthalpy of formation of CO<sub>2</sub> is more than that of Al<sub>2</sub>O<sub>3</sub>
- (c) Pure carbon is not easily available
- (d) The enthalpy of formation of Al<sub>2</sub>O<sub>3</sub> is too high

6. In which of the following isolations no reducing agent is required?

- (a) Iron from haematite
- (b) Aluminium from bauxite
- (c) Mercury from cinnabar
- (d) Zinc from zinc blende

7. Which of the following are methods of concentration of metals?

- (a) Gravity separation
- (b) Froth flotation process
- (c) Electromagnetic separation
- (d) Smelting

8. Boron can be obtained by various methods but not by

- (a) thermal decomposition of B<sub>2</sub>H<sub>6</sub>
- (b) pyrolysis of BI<sub>3</sub> (van Arkel)
- (c) reducing BCl<sub>3</sub> with H<sub>2</sub>
- (d) electrolysis of fused BCl<sub>3</sub>

9. Following method is not used for extraction of Al

- (a) van Arkel
- (b) Serpeck
- (c) Baeyer
- (d) Hall-Heroult

10. Roasting is carried out to

- (a) convert sulphide to oxide and sulphate
- (b) remove water of hydration
- (c) melt the ore
- (d) remove arsenic and sulphur impurities

$$\Delta G_f^\circ \text{ for CuO} = 129.7 \text{ kJ mol}^{-1}, \text{CO} = -137.2 \text{ kJ mol}^{-1}$$

$$\text{H}_2\text{O} = -237.2 \text{ kJ mol}^{-1}$$

3. Copper pyrites, CuFeS<sub>2</sub>, is the important source of copper. 10 g of it was leached with dil. H<sub>2</sub>SO<sub>4</sub> and solution diluted to 1 L.

- (a) 10 mL of this solution required 10 mL of 0.02 M KMnO<sub>4</sub> in acidic solution
- (b) 10 mL of this solution was treated with excess KI and liberated I<sub>2</sub> required 10 mL of 0.02 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. (Cu = 63.5, Fe = 56)

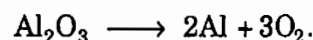
What is % of Fe and Cu in CuFeS<sub>2</sub>?

4. Use the relationship  $\Delta G^\circ = -nFE_{\text{cell}}^\circ$  to estimate the minimum voltage required to electrolyse Al<sub>2</sub>O<sub>3</sub> in the Hall-Heroult process.

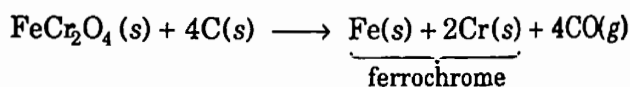
$$\Delta G_f^\circ(\text{Al}_2\text{O}_3) = -1520 \text{ kJ mol}^{-1}$$

$$\Delta G_f^\circ(\text{CO}_2) = -394 \text{ kJ mol}^{-1}$$

Show that the oxidation of the graphite anode to CO<sub>2</sub> permits the electrolysis to occur at a lower voltage than if the electrolysis reactions were



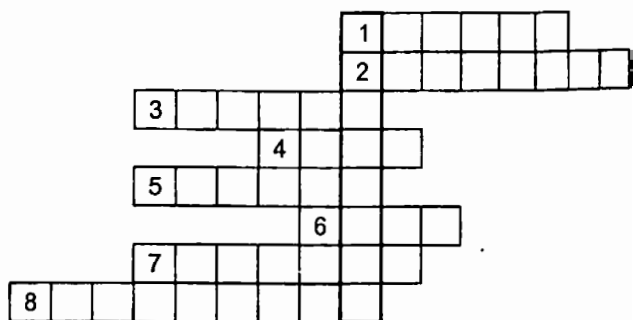
5. Ferrochrome, an iron-chromium alloy used in making stainless steel, is produced by reducing chromite (FeCr<sub>2</sub>O<sub>4</sub>) with coke



- (a) How many kilograms of chromium can be obtained by the reaction of 236 kg of chromite with an excess of coke?
- (b) How many litres of carbon monoxide at 25°C and 740 mm Hg are obtained as a by-product? (Cr = 52, Fe = 56, C = 12, O = 16)

6. Complete the following puzzle-crossword

Metals and activity series crossword. 1. Displaces silver but not lead. 2. Honorary metal in many versions of the activity series. 3. Unreactive metal, a salt of which is used in the chloride test. 4. Most abundant transition metal in Earth's crust. 5. This metal forms a nitrate which is hard to decompose. 6. Metal used in sacrificial protection of iron from corrosion. 7. First member of Group IA element. 8. This metal does not react with water, but reacts with acid.



## Brain Twisters

1.  $E_{\text{Fe}^{2+}/\text{Fe}}^\circ = 0.44 \text{ V}$ ,  $E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.34 \text{ V}$ ,  $E_{\text{Ag}^+/\text{Ag}}^\circ = 0.80 \text{ V}$

Will Fe displace Cu from CuSO<sub>4</sub> solution?

Will Ag displace Cu from CuSO<sub>4</sub> solution?

2. CuO can't be reduced by carbon but can be reduced by H<sub>2</sub>. Explain in terms of thermodynamics, given :

7. 18.4 g of a mixture of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  on strongly heating gave 8.8 g of  $\text{CO}_2$  gas. Calculate mole% of each in the mixture.

## Passage Comprehension Questions

### Passage 1

Read the following short write-up about recovery of magnesium and answer the questions at the end of it.

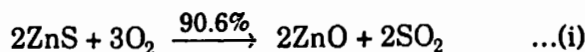
Magnesium is a valuable, light weight metal used as a structural material as well as in alloys, in batteries, and in chemical synthesis. Although magnesium is plentiful in Earth's crust, it is cheaper to mine the metal from sea-water. Magnesium forms the second most abundant cation in the sea (after sodium); there are about 1.3 g of magnesium in a kilogram of sea-water. The process for obtaining magnesium from sea-water employs all three types of reactions precipitation, acid-base, and redox reactions.

- Precipitation reaction involves formation of
  - insoluble  $\text{MgCO}_3$  by adding  $\text{Na}_2\text{CO}_3$
  - insoluble  $\text{Mg}(\text{OH})_2$  by adding  $\text{Ca}(\text{OH})_2$
  - insoluble  $\text{MgSO}_4$  by adding  $\text{Na}_2\text{SO}_4$
  - insoluble  $\text{MgCl}_2$  by adding  $\text{NaCl}$
- Acid-base reaction involves reaction between
  - $\text{MgCO}_3$  and  $\text{HCl}$
  - $\text{Mg}(\text{OH})_2$  and  $\text{H}_2\text{SO}_4$
  - $\text{Mg}(\text{OH})_2$  and  $\text{HCl}$
  - $\text{MgCO}_3$  and  $\text{H}_2\text{SO}_4$
- Redox reaction takes place (in the extraction of Mg)
  - in the electrolytic cell when fused  $\text{MgCl}_2$  is subjected to electrolysis
  - when fused  $\text{MgCl}_2$  is heated
  - when fused  $\text{MgCO}_3$  is strongly heated
  - none of the above
- Instead of calcium oxide, why don't we simply add sodium hydroxide to sea-water to precipitate magnesium hydroxide?
  - Solubility of  $\text{Ca}(\text{OH})_2$  is smaller than that of  $\text{NaOH}$  so that  $\text{Mg}(\text{OH})_2$  is precipitated
  - $\text{NaOH}$  may dissolve  $\text{Mg}(\text{OH})_2$  formed
  - $\text{NaOH}$  may also precipitate other species, being a strong electrolyte
  - $\text{NaOH}$ , being a weak electrolyte will not coagulate  $\text{Mg}(\text{OH})_2$
- Which is the best source of the given process in the metallurgical process?
  - Magnesite
  - Kieserite
  - Epsomite
  - Dolomite

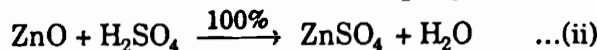
### Passage 2

Following passage describes extraction of zinc from zinc sulphide. Answer the questions at the end of it.

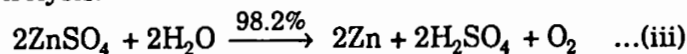
The chief ore of zinc is the sulphide,  $\text{ZnS}$ . The ore is concentrated by flotation process and then heated in air, which converts the  $\text{ZnS}$  to  $\text{ZnO}$ .



The  $\text{ZnO}$  is then treated with dilute  $\text{H}_2\text{SO}_4$



to produce  $\text{ZnSO}_4(\text{aq})$  which produces  $\text{Zn}$  metal on electrolysis.

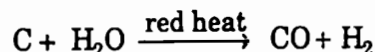


- What mass of  $\text{Zn}$  will be obtained from an ore containing 225 kg of  $\text{ZnS}$ ? Efficiencies of the process have been indicated above the arrow mark. ( $\text{Zn} = 65, \text{S} = 32, \text{O} = 16, \text{H} = 1$ )
  - 134 kg
  - 112 kg
  - 102 kg
  - 130 kg
- What amount of current is required (with 100% efficiency) in step (iii) if it takes one month?
  - 10.2 A
  - 15.4 A
  - 17.0 A
  - 154.0 A
- $\text{ZnO}$  in step (ii) can also be dissolved in  $\text{NaOH}$  forming
  - $\text{Zn}(\text{OH})_2$
  - $\text{Na}_2\text{ZnO}_2$
  - $\text{Zn}_2\text{O}_3$
  - $\text{NaZn}(\text{OH})_4$
- How many kilomoles of  $\text{NaOH}$  are required to dissolve all the  $\text{ZnO}$  of step (i) assuming 100% yield?
  - 2.32
  - 1.16
  - 4.64
  - 9.28
- What volume of 98%  $\text{H}_2\text{SO}_4$  (by weight, density 1.8 g/mL) is required in step (ii) assuming 100% yield of steps (i) and (ii)
  - 130 L
  - 140 L
  - 120 L
  - 150 L

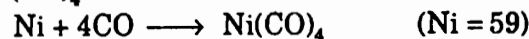
### Passage 3

Questions given below are based on the following sequence of reactions:

At high temperature carbon reacts with water to produce a mixture of carbon monoxide ( $\text{CO}$ ) and hydrogen ( $\text{H}_2$ ).



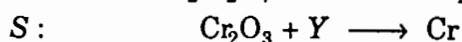
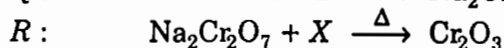
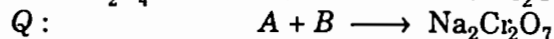
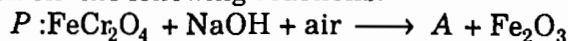
$\text{CO}$  is separated from  $\text{H}_2$ , and then used to separate nickel from cobalt by forming a volatile compound, nickel tetracarbonyl,  $\text{Ni}(\text{CO})_4$ .



- How many moles of  $\text{Ni}(\text{CO})_4$  could be obtained from the  $\text{CO}$  produced by the reaction of 75.0 g of carbon? Assume 100% reaction and 100% recovery in both steps.
  - 6.25
  - 1.563
  - 3.125
  - 25.0
- Formation of volatile  $\text{Ni}(\text{CO})_4$  and its subsequent heating gives pure  $\text{Ni}$ . This process is called
  - Hall
  - Dow
  - Serpeck
  - Mond

### Passage 4

$\text{FeCr}_2\text{O}_4$  (chromite) is a good source of chromium and its compounds like  $\text{Na}_2\text{CrO}_4$ ,  $\text{Na}_2\text{Cr}_2\text{O}_7$ . Questions are based on the following reactions.



- Compounds (A) and (B) are
  - $\text{Na}_2\text{CrO}_4, \text{H}_2\text{SO}_4$
  - $\text{Na}_2\text{Cr}_2\text{O}_7, \text{HCl}$
  - $\text{Na}_2\text{CrO}_5, \text{H}_2\text{SO}_4$
  - $\text{Na}_4[\text{Fe}(\text{OH})_6], \text{H}_2\text{SO}_4$
- (X) and (Y) are
  - Al and C
  - C and Al
  - C in both
  - Al in both
- $\text{Na}_2\text{CrO}_4$  and  $\text{Fe}_2\text{O}_3$  are separated by
  - dissolving in conc.  $\text{H}_2\text{SO}_4$
  - dissolving in  $\text{NH}_3$
  - dissolving in  $\text{H}_2\text{O}$
  - dissolving in dil. HCl

### Passage 5

Questions given below are based on the Periodic Table showing different ores/minerals.

|    |    |    |    |    |    |      |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|------|----|----|----|----|----|----|----|----|----|----|----|
| 1  |    |    |    |    |    |      |    |    |    |    |    |    |    |    |    |    | 18 |
|    | 2  |    |    |    |    |      |    |    |    |    |    | 13 | 14 | 15 | 16 | 17 |    |
| Li | Be |    |    |    |    |      |    |    |    |    |    |    |    |    |    |    |    |
| Na | Mg | 3  | 4  | 5  | 6  | 7    | 8  | 9  | 10 | 11 | 12 | Al |    |    |    |    |    |
| K  | Ca | Sc | Ti | V  | Cr | Mn   | Fe | Co | Ni | Cu | Zn | Ga |    |    |    |    |    |
| Rb | Sr | Y  | Zr | Nb | Mo | (Tc) | Ru | Rh | Pd | Ag | Cd | In | Sn |    |    |    |    |
| Cs | Ba | La | Hf | Ta | W  | Re   | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi |    |    |    |



Chlorides Silicates Carbonates Phosphates Oxides Free metals Sulphides

Primary mineral sources of metals. The *s*-block metals occur as chloride, silicates, and carbonates. The *d*- and *p*-block metals are found as oxides and sulphides, except for the group 3, metals, which occur as phosphates, and the platinum group metals and gold, which occur in uncombined form. There is no mineral source of technitium (Tc in group 7), a radioactive element that is made in nuclear reactors.

1. The early transition metals on the left hand side of the *d*-block generally occur as oxides because
  - (a) they are above hydrogen in electrochemical series
  - (b) they are more electropositive and thus form ionic compounds (in the form of oxides) by more electronegative oxygen by exchange of electrons
  - (c) these oxides are soluble in water
  - (d) these oxides remain insoluble in water
2. Transition metals on the right hand side of the *d*-block occurs as sulphides because of
  - (a) their high electronegativity values as a result of which covalent sulphides are formed

- (b) their much low electronegativity values as a result of which ionic sulphides are formed
  - (c) high melting point of sulphides
  - (d) low melting point of sulphides
3. *s*-block elements generally occurs as carbonates and silicates (as  $\text{MgCO}_3$ ,  $\text{CaSiO}_3$ ) because
- (a) these elements react with  $\text{CO}_2$  and  $\text{SiO}_2$
  - (b) these elements are decomposed by acid reacts
  - (c) their oxides are basic and oxides react with acidic oxides in an acid-base reactions
  - (d) their oxides are acidic and oxides react with basic oxides in an acid-base reaction
4. Elements found in native state are
- (a) Pb and Bi as they are in *p*-block
  - (b) Hg and Os as they are in liquid state
  - (c) C and Si as they are non-metals
  - (d) Pt and Au as they are at the bottom of the electrochemical series

### Passage 6

Questions given below are based on the natural occurring minerals/ores.

Look at the location of elements *A*, *B*, *C* and *D* in the following Periodic Table and answer the questions given below

A simplified periodic table grid is shown. The grid consists of 18 columns and 4 rows. The first two columns are filled with 8 elements each (4 in the first row, 3 in the second, 2 in the third, and 1 in the fourth). The next 10 columns (columns 3-12) are empty. The last two columns (columns 13-14) are filled with 8 elements each (4 in the first row, 3 in the second, 2 in the third, and 1 in the fourth). The elements are marked as follows: C is in the first column, third row; A is in the third column, second row; B is in the twelfth column, second row; and D is in the tenth column, third row.

[illegible]

1. Which of the elements indicated by *A*, *B*, *C* and *D* is expected to be found in native state?  
(a) *A* (b) *B*  
(c) *C* (d) *D*
2. Which is found as its sulphide?  
(a) *A* (b) *B*  
(c) *C* (d) *D*
3. Which is found as its carbonate?  
(a) *A* (b) *B*  
(c) *C* (d) *D*
4. Which is found as its oxide?  
(a) *A* (b) *B*  
(c) *C* (d) *D*
5. Imagine a planet with an atmosphere that contains  $O_2$  and  $SO_2$  but no  $CO_2$ . What is the chemical composition of the mineral you would expect to find for the alkaline earth metals (*M*) on such a planet?  
(a)  $MO_2, M_2O_2$  (b)  $MSO_3, MSO_4$   
(c)  $M(HSO_3)_2, M(HSO_4)_2$  (d) all of these

### Passage 7

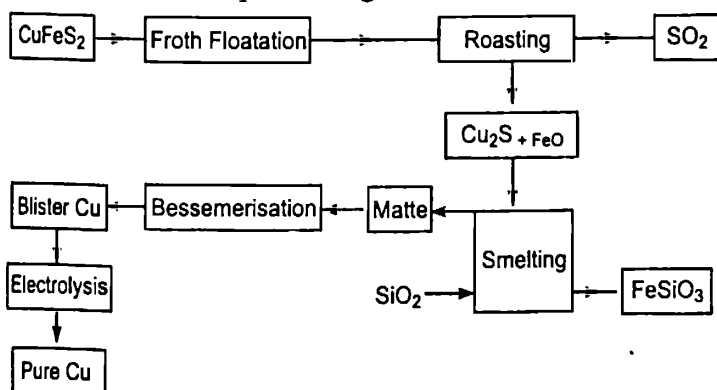
Read the following cyclic process of recovery of copper from a copper wire and answer the questions at the end of it.

The following cycle of copper experiment is performed in some general chemistry laboratories. The series of reactions starts with copper and ends with metallic copper. The steps are as follows: (1) A piece of copper wire of known mass is allowed to react with concentrated nitric acid [the products are copper(II) nitrate, nitrogen dioxide, and water]. (2) The copper (II) nitrate is treated with a sodium hydroxide solution to form copper (II) hydroxide precipitate. (3) On heating copper (II) hydroxide decomposes to yield copper (II) oxide. (4) The copper (II) oxide is reacted with concentrated sulphuric acid to yield copper (II) sulphate. (5) Copper(II) sulphate is treated with an excess of zinc metal to form metallic copper. (6) The remaining zinc metal is removed by treatment with hydrochloric acid, and metallic copper is filtered, dried, and weighted. (Cu = 63.5)

- Assuming that a student started with 65.6 g of copper, calculate the theoretical yield of copper sulphate  
(a) 165 g (b) 82.4 g  
(c) 90 g (d) 100.2 g
- Copper obtained at the end of the cycle is ..... amount originally taken  
(a) less than  
(b) greater than  
(c) nearly equal  
(d) only copper salts are obtained
- $\text{CuSO}_4$  solution thus formed is subjected to electrolysis. To deposit all the copper formed at the end, a current of 50 A will have to be used for approximately  
(a) 10 h (b) 1 h  
(c) 5 h (d) 0.5 h

### Passage 8

Given flow-sheet is for the extraction of copper. Based on this, answer the questions given at the end

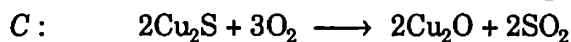
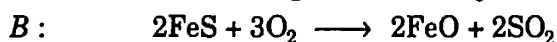
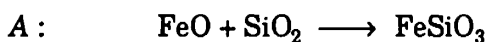


- Froth-flotation process can be made more effective by  
(a) use of pine oil which produces stable froth

- use of sodium ethyl xanthate as a collector that coats the particles of ore
- both (a) and (b)
- none of the above

- Smelting process is carried at about  $1400^\circ\text{C}$ . Two layers are formed  
(a) Bottom layer contains copper-matte  
(b) Upper layer contains copper-matte  
(c) Copper-matte remains in both the layers  
(d) Copper-matte is not present in any of the layers

- Some of the reactions taking place during bessemerisation are

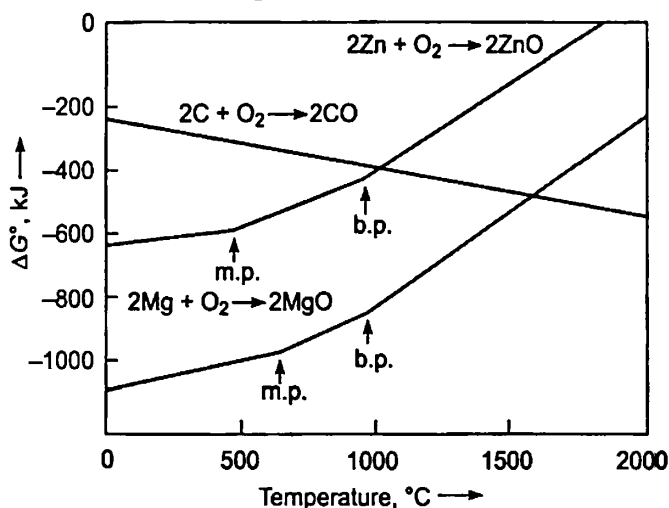


Select reactions actually taking place

- A, B
  - B, C
  - A, C
  - C, D
- In the electrorefining method  
(a) anode is pure copper  
(b) anode is impure copper  
(c) anode mud contains noble metals  
(d) cathode mud contains noble metals
  - This method is called  
(a) pyrometallurgical (b) hydrometallurgical  
(c) parametallurgical (d) semimetallurgical

### Passage 9

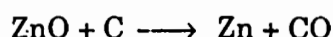
Questions given below are based on the given diagram for extractive metallurgy.



The points noted by arrows are the melting and boiling points of the metals zinc and magnesium.  $\Delta G^\circ$  as a function of temperature for some reactions of extractive metallurgy.

- At what approximate temperature, zinc and carbon have equal affinity for oxygen?  
(a)  $1000^\circ\text{C}$  (b)  $1500^\circ\text{C}$   
(c)  $500^\circ\text{C}$  (d)  $1200^\circ\text{C}$

2. At this temperature  $\Delta G^\circ$  of the reaction is



- (a) -ve (b) +ve  
(c) zero (d) nothing can be said

3. To make the following reduction process spontaneous, temperature should be



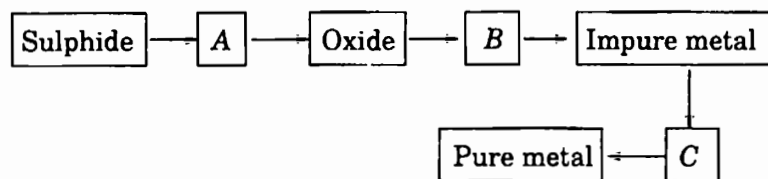
- (a)  $< 1000^\circ\text{C}$   
(b)  $> 1100^\circ\text{C}$   
(c)  $< 500^\circ\text{C}$   
(d)  $> 500^\circ\text{C}$  but  $< 1000^\circ\text{C}$

4. At  $1100^\circ\text{C}$ , which reaction is spontaneous to a maximum extent?

- (a)  $\text{MgO} + \text{C} \longrightarrow \text{Mg} + \text{CO}$   
(b)  $\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}$   
(c)  $\text{MgO} + \text{Zn} \longrightarrow \text{Mg} + \text{ZnO}$   
(d)  $\text{ZnO} + \text{Mg} \longrightarrow \text{MgO} + \text{Zn}$

### Passage 10

From the following flow-sheet for the extraction of pure metal, answer the questions at the end of it.



- Step A is
  - roasting
  - smelting
  - calcination
  - bessemerisation
- Step B (reduction) can be carried out using
  - carbon
  - more electropositive element
  - both (a) and (b)
  - none of the above
- Impure Cu metal is also obtained
  - by self reduction during roasting of CuS
  - by reduction of CuO with  $\text{H}_2$
  - by reduction of CuO with Al
  - by electrolysis of  $\text{Cu}^{2+}$  solution
- Some of the following metals are obtained by electrolysis of their fused salts  
Al, Na, Cu, Ag, Mg, Ca. These metals are
  - Cu, Ag
  - Al, Na, Cu
  - Ag, Mg, Ca
  - Al, Na, Mg, Ca
- Reduction of oxides to elements with carbon generally takes place at high temperature, hence Al is used in aluminothermite process. It is because
  - Al is more electropositive than the other metals (to be formed by reduction)
  - Al has maximum affinity for oxygen
  - reduction is highly exothermic and heat liberated makes the process spontaneous

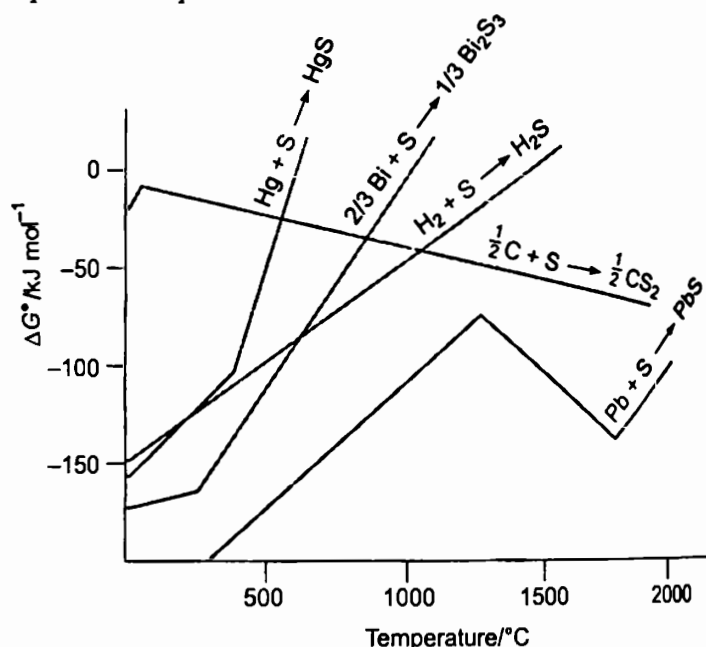
(d) reduction is highly endothermic and heat absorbed makes the process spontaneous.

6. Following reaction is not involved in Thermite process

- (a)  $3\text{Mn}_3\text{O}_4 + 8\text{Al} \longrightarrow 9\text{Mn} + 4\text{Al}_2\text{O}_3$   
(b)  $\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$   
(c)  $2\text{Fe} + \text{Al}_2\text{O}_3 \longrightarrow 2\text{Al} + \text{Fe}_2\text{O}_3$   
(d)  $\text{B}_2\text{O}_3 + 2\text{Al} \longrightarrow 2\text{B} + \text{Al}_2\text{O}_3$

### Passage 11

The Ellingham diagram for a number of metallic sulphides is reproduced below.



Answer the questions given below

- Formation of which of the sulphides is most spontaneous?
  - HgS
  - $\text{Bi}_2\text{S}_3$
  - PbS
  - $\text{CS}_2$
- Which occurs to minimum extent in nature?
  - HgS
  - $\text{H}_2\text{S}$
  - $\text{Bi}_2\text{S}_3$
  - $\text{CS}_2$
- Which of the following sulphides can be reduced to metal by  $\text{H}_2$  at about  $1000^\circ\text{C}$ ?
  - HgS
  - PbS
  - $\text{Bi}_2\text{S}_3$
  - All of these

### Assertion & Reason

Codes :

- (a) Both A and R are true and R is the correct explanation of A.  
(b) Both A and R are true but R is not the correct explanation of A.  
(c) A is true but R is false.  
(d) A is false but R is true.  
(e) A and R both are false.

1. **Assertion (A)** : Gold occurs in native state.

**Reason (R)** : Gold dissolves in aqua-regia.

2. **Assertion (A)** : Froth-flotation process is used to concentrate sulphide ores.

**Reason (R)** : There is difference in the wettability of different minerals.

3. **Assertion (A)** :  $\text{Al}_2\text{O}_3$  is converted into Al by reduction with carbon.

**Reason (R)** : Carbon (graphite) has greater affinity for oxygen than aluminium has.

4. **Assertion (A)** : Metals of high impurity are obtained by zone-refining.

**Reason (R)** : Impurities in the ore are more soluble in the melt than in the pure metal.

5. **Assertion (A)** : Reduction of ZnO with carbon is done at  $1100^\circ\text{C}$ .

**Reason (R)** : At this temperature,  $\Delta G^\circ$  is negative thus process is spontaneous.

6. **Assertion (A)** : Desilverisation of lead is done by Parke's method.

**Reason (R)** : When lead-silver alloy is poor in silver, zinc is added to molten ore.

17. Sulphide ore is converted into pure metal (say Cu) by following steps.

Bessemerisation  $\longrightarrow$  Roasting  $\longrightarrow$  Electrolysis

18. Dow sea-water process is used for the extraction of Mg.

19.  $\text{FeWO}_4$  and  $\text{MnWO}_4$  are magnetic impurities.

20. Calcium silicate is called cementite.

## Fill in the Blanks

1. When  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  is heated, green coloured residue is ..... along with gas .....

2. The reducing agent used in thermite process is .....

3. In cyanide process, Zn is added to soluble ..... to get Ag.

4. Temperature required in pyrometallurgical process is ..... than that required in hydrometallurgical process.

5. .... iron is the purest form of it.

6. .... iron is brittle.

7. Most abundant element in the earth's crust is .....

8. Most abundant metal in the earth's crust is .....

9. Sulphur is extracted by .....

10.  $\text{ZrI}_4$  is converted to Zr by the .....

11. Mg can be used to reduce  $\text{TiCl}_4$  into Ti in .....

12. Self-reduction process is used in the extraction of ..... and lead.

13. Dow sea-water process is used in extraction of .....

14. In Serpeck process, bauxite is converted into ..... which is hydrolysed to precipitate .....

15. Cryolite,  $\text{Na}_3\text{AlF}_6$  is added to  $\text{Al}_2\text{O}_3$  in ..... process to ..... m.p. and to ..... electrical conductivity.

16. Parke's process is used to separate ..... from argentiferous lead.

17.  $\text{Be}_2\text{C}$  and  $\text{Al}_4\text{C}_3$  are also called ..... because they react with  $\text{H}_2\text{O}$  yielding .....

18. CO is toxic because it forms complex with ..... in the blood.

19. When  $\text{FeCr}_2\text{O}_4$  is heated with carbon an alloy called ..... is obtained.

20.  $\text{FeS}_2$  is also called ..... because it has been mistaken for gold.

## True & False

1. Lunar caustic is KOH.

2. KCN forms soluble complex with silver glance.

3. Zinc can displace silver from  $[\text{Ag}(\text{CN})_2]^-$ .

4. Main source of aluminium is corundum.

5. Wrought iron is prepared by Pudding process.

6. Pig iron is the purest form of iron.

7. Steel is mostly made by BOP method.

8. Heating the steel to appropriate temperature for a short time and then cooling it rapidly in order to give it the desired mechanical properties is called the tempering.

9. Oxides of the s-block metals are strongly acidic and form salts with basic oxides.

10. Oxygen is the most abundant metal on the earth's crust.

11. Mond's process is used for the extraction of Mg.

12. In the bessemerisation of sulphide ore of copper, there is self-reduction giving copper metal.

13. Na is obtained by the electrolysis of aqueous NaCl solution.

14. Al is obtained by the electrolysis of fused mixture of  $\text{Al}_2\text{O}_3$  and  $\text{Na}_3\text{AlF}_6$ .

15. Metals of high purity (to be used in semiconductors) are obtained by zone-refining.

16. Concentration of sulphide ore is done by calcination method.

21. '18 carat' gold is ..... pure.
22. 'Puddling' process was used originally to make .....
23. Puddling process involved mixing molten ..... iron with haematite and burning off all the C and other impurities to give ..... iron.
24. BOP is the modern process to prepare .....
25. Siemen open-hearth process is used in making .....
26. Mond's process is used in the extraction of .....
27.  $\text{Cu}_2\text{S}$  is called .....
28. Malachite (green) is .....
29. Zinc is used to extract silver by solvent extraction from molten lead in ..... process
30. Paris green is ..... made from basic copper acetate, arsenious oxide and acetic acid.

## Matrix-Match Type Questions

### I. Only One Correct

1. Match the compounds (in List I) with their applications/colours (in List II).

| List I                                              | List II                    |
|-----------------------------------------------------|----------------------------|
| A. $\text{Pb}_3\text{O}_4$                          | 1. White lead              |
| B. $(\text{PbCO}_3)_2 \cdot \text{Pb}(\text{OH})_2$ | 2. Rust proofing sheets    |
| C. $\text{Ca}_2\text{PbO}_4$                        | 3. Road signs and markings |
| D. $\text{PbCrO}_4$                                 | 4. Red lead                |

2. Match the reactions taking place in blast furnace (in List I) with temperature-range of operations (in List II).

| List I                                                                         | List II                 |
|--------------------------------------------------------------------------------|-------------------------|
| A. $\text{Fe}_2\text{O}_3 + \text{CO} \longrightarrow \text{CO}_2 + \text{Fe}$ | 1. $1200^\circ\text{C}$ |
| B. $\text{C} + \text{CO}_2 \longrightarrow \text{CO}$                          | 2. $900^\circ\text{C}$  |
| C. $\text{C} + \text{H}_2\text{O} \longrightarrow \text{CO} + \text{H}_2$      | 3. $600^\circ\text{C}$  |
| D. $\text{CaO} + \text{SiO}_2 \longrightarrow \text{CaSiO}_3$                  | 4. $1100^\circ\text{C}$ |

3. Match process (in List I) with electrolytes (in List II).

| List I                   | List II                                                      |
|--------------------------|--------------------------------------------------------------|
| A. Downs cell            | 1. Fused $\text{MgCl}_2$                                     |
| B. Dow sea-water process | 2. Fused $(\text{Al}_2\text{O}_3 + \text{Na}_3\text{AlF}_6)$ |
| C. Hall-Heroult          | 3. Fused $\text{KHF}_2$                                      |
| D. Moissan               | 4. Fused $(40\% \text{NaCl} + 60\% \text{CaCl}_2)$           |

4. Match ores in List I with metals in List II.

| List I          | List II      |
|-----------------|--------------|
| A. Carnallite   | 1. Zinc      |
| B. Calamine     | 2. Titanium  |
| C. Ilmenite     | 3. Magnesium |
| D. Chalcopyrite | 4. Copper    |

5. Match the extraction process listed in List I with metals listed in List II.

| List I                                         | List II      |
|------------------------------------------------|--------------|
| A. Self reduction                              | 1. Zirconium |
| B. Carbon reduction                            | 2. Silver    |
| C. Complex formation and displacement by metal | 3. Copper    |
| D. Decomposition of iodide                     | 4. Boron     |

6. Match the method in List I with related reaction in List II.

| List I                       | List II                                                                                         |
|------------------------------|-------------------------------------------------------------------------------------------------|
| A. Mond's process            | 1. $\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$      |
| B. van Arkel-de-Boer process | 2. $\text{TiCl}_4 + \text{Mg} \xrightarrow{1000-1150^\circ\text{C}} \text{Ti} + 2\text{MgCl}_2$ |
| C. Thermite process          | 3. $\text{Ni}(\text{CO})_4 \xrightarrow{230^\circ\text{C}} \text{Ni} + 4\text{CO}$              |
| D. Kroll process             | 4. $2\text{CuO} + \text{CuS} \longrightarrow 3\text{Cu} + \text{SO}_2$                          |
| E. Self reduction            | 5. $\text{ZrI}_4 \xrightarrow{\Delta} \text{Zr} + 2\text{I}_2$                                  |

### II. One or More Correct

1. Match the species in Column I with then corresponding methods of extraction/concentration in Column II.

| List I            | List II                                     |
|-------------------|---------------------------------------------|
| A. Copper pyrites | 1. Electrolysis                             |
| B. Galena         | 2. Mac-Arthur Forrest method                |
| C. Silver glance  | 3. Extraction by complex formation          |
| D. Corundum       | 4. Magnetic separation                      |
| E. Ilmenite       | 5. Concentration by gravity separation      |
|                   | 6. Concentration by froth-flotation process |

2. Match the elements in Column I with their corresponding mineral formation in Column II.

| List I       | List II      |
|--------------|--------------|
| A. Calcium   | 1. Oxide     |
| B. Copper    | 2. Sulphide  |
| C. Magnesium | 3. Phosphate |
| D. Silver    | 4. Carbonate |
| E. Aluminium | 5. Chloride  |
|              | 6. Fluoride  |
|              | 7. Sulphate  |



The grid-in response area consists of two rows of 15 boxes each. The top row has five bubbles labeled A, B, C, D, and E. The bottom row is empty.



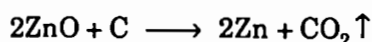
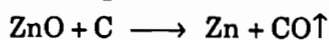
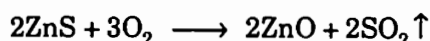
# Answers & Solutions

## Master Exercises

### Exercise 1

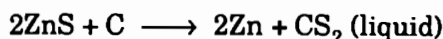
#### Short Answer Type Questions

1. In practice, sulphide ore is first roasted in air to the corresponding oxide which in turn is reduced to metal with carbon.

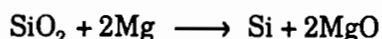


CO, CO<sub>2</sub> and SO<sub>2</sub> being gases escape from the reaction and thus, entropy change is positive and reaction is thermodynamically favourable.

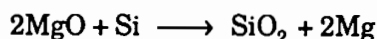
If ZnS is directly reduced with carbon, CS<sub>2</sub> (liquid) is formed which remain in reaction mixture. Entropy change is less positive and reaction is thermodynamically less favourable.



2. (i) Reaction (a) since gaseous species (CO, SO<sub>2</sub>) escape from the mixture  
(ii) Reaction (a)  
(iii) Reaction (a)
3. In the Ellingham diagram, below 2000 K magnesium curve is below the silicon curve. Above 2000 K, the silicon curve lies lower than the magnesium curve. Thus, magnesium can reduce silicon dioxide to silicon below 2000 K.



Silicon can reduce magnesium oxide above 2000 K



4. (a) FeWO<sub>4</sub> (b) MnWO<sub>4</sub>

5. A : SnSO<sub>4</sub> in dil. H<sub>2</sub>SO<sub>4</sub>

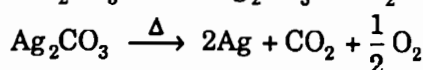
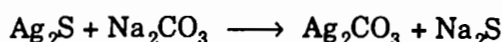
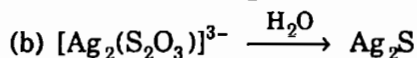
B : Blocks of impure tin

C : Sheet of pure tin

6. (a) Silver is present as

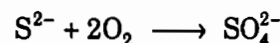
(i) soluble [Ag(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>]<sup>3-</sup>

(ii) insoluble AgBr

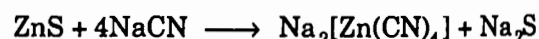


- (c) AgBr and Ag<sub>2</sub>S

7. Air is passed when S<sup>2-</sup> is oxidised to SO<sub>4</sub><sup>2-</sup>



8. Add NaCN. ZnS changes to soluble complex



PbS can now be enriched by froth flotation process without affecting ZnS.

9. (a) Mineral containing silver and lead is melted, and molten zinc is added. Ag is distributed between zinc and lead layers (zinc being lighter forms upper layer). Since, solubility of Ag in molten zinc is higher than in molten lead, hence, most of the silver goes from lead layer to zinc layer. Two layers are separated. Ag containing zinc layer is distilled when zinc separates leaving behind silver.

(b) Parke's method.

10. (a) Basic oxygen process

(b) (i) pig iron (ii) cast iron (iii) wrought iron

(c) wrought iron

11. Forward reaction is endothermic so that formation of cementite (Fe<sub>3</sub>C) is favoured at high temperatures. When steel containing Fe<sub>3</sub>C is cooled slowly, equilibrium is displaced in left hand side and the carbon separates. If the steel is cooled rapidly, equilibrium is not attained and the carbon remains in the form of Fe<sub>3</sub>C.

#### Analytical Questions

1. (a)  $\Delta G^\circ = \Delta G_f^\circ (\text{products}) - \Delta G_f^\circ (\text{reactants})$

$$\text{(I) } \Delta G^\circ (\text{element}) = 0$$

$$\Delta G^\circ = \Delta G^\circ (\text{CS}_2) - 2\Delta G^\circ (\text{CuS})$$

$$= 63.6 - 2(-49)$$

$$= 161.6 \text{ kJ mol}^{-1}$$

$$\text{(II) } \Delta G^\circ = 2703.6 \text{ kJ mol}^{-1}$$

- (b) If  $\Delta G^\circ = -ve$  then spontaneous (→)

= +ve then non-spontaneous (←)

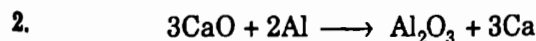
$$\text{(III) } \Delta G_f^\circ = -757.2 \text{ kJ mol}^{-1}$$

- (c) Formation of SO<sub>2</sub> is more spontaneous

$$\text{(d) } \Delta G = \Delta H - T\Delta S$$

If T is low, ΔS is also low such that TΔS < ΔH making ΔG positive hence, non-spontaneous.

At higher temperature, reactions are spontaneous.

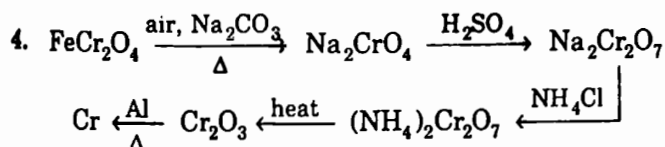


$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ(\text{Al}_2\text{O}_3) - 3\Delta G_f^\circ(\text{CaO}) \\ &= -1582 + 1812.6 \\ &= +ve\end{aligned}$$

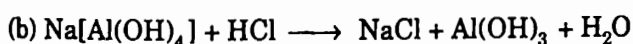
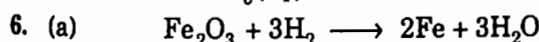
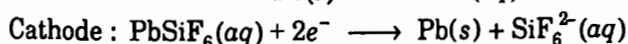
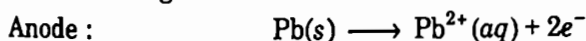
hence non-spontaneous.

Student was wrong.

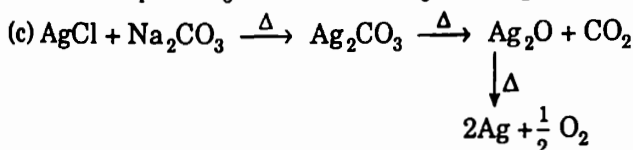
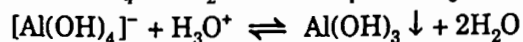
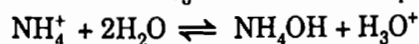
3. Au dissolves in aqua-regia (1 part conc.  $\text{HNO}_3$  and 3 parts conc.  $\text{HCl}$ ) forming soluble  $\text{HAuCl}_4$ , but Ag forms insoluble  $\text{AgCl}$ .



5. The impure lead metal serves as the anode and pure lead serves as the cathode. Impurities either remain at the anode or go into solution.

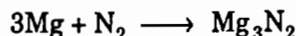


but strong acid like  $\text{HCl}$  will further dissolve  $\text{Al}(\text{OH})_3$  which is amphoteric. Aqueous solution of  $\text{NH}_4\text{Cl}$  is slightly acidic and this acidic solution will cause precipitation of  $\text{Al}(\text{OH})_3$  from  $\text{Na}[\text{Al}(\text{OH})_4]$

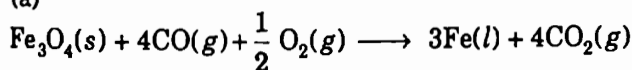


7. Since,  $E^\circ < 0$  for  $\text{Zn}^{2+}$ ; the reduction of  $\text{Zn}^{2+}$  is not favoured. Since,  $E^\circ > 0$  for  $\text{Hg}^{2+}$ , the reduction of  $\text{Hg}^{2+}$  is favoured. The roasting of  $\text{CdS}$  should give  $\text{CdO}$  since  $E^\circ < 0$  for  $\text{Cd}^{2+}$ .

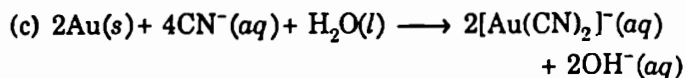
8. Since,  $\text{N}_2$  can also combine with  $\text{Mg}$  giving magnesium nitride, and inert atmosphere no longer remains



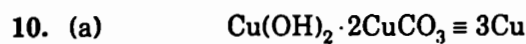
9. (a)



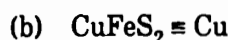
(b) balanced



(c) is used to convert mineral to a free metal



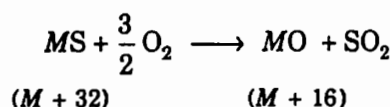
$$\begin{aligned}344.5 \text{ g} &\equiv 3 \times 63.5 \text{ g Cu} \\ 0.033 \text{ g} &= \frac{3 \times 63.5 \times 0.033 \text{ g}}{344.5} \text{ Cu} = 0.0182 \text{ g}\end{aligned}$$



$$\begin{aligned}183.5 \text{ g} &\equiv 63.5 \text{ g} \\ 0.0495 \text{ g} &= \frac{63.5 \times 0.0495}{183.5} \text{ g Cu} = 0.0171 \text{ g}\end{aligned}$$

(a) gives greater quantity of ore

11. Sulphide is =  $\text{MS}$  (oxidation number of metal ion being +2)



$$\begin{array}{cc} (M + 32) & (M + 16) \end{array}$$

$$1.164$$

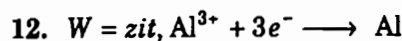
$$0.972$$

$$\frac{M + 32}{1.164} = \frac{M + 16}{0.972}$$

$\therefore$

$\therefore$

$$M = 64$$



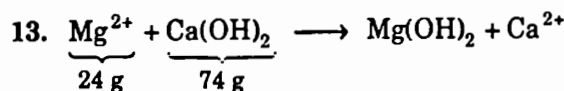
where,  $z = \text{electrochemical equivalent}$   
 $= \frac{\text{atomic mass}}{\text{electrons} \times 96500} = \frac{27}{3 \times 96500}$

$$i = \text{current (A)} = 94.0 \text{ A}$$

$$t = \text{time (seconds)} = 1 \text{ h} = 3600 \text{ s}$$

$$\therefore w = \frac{9 \times 94 \times 3600}{96500}$$

$$= 31.56 \text{ g}$$



$$1272 \text{ g} \quad ?$$

$$24 \text{ g of } \text{Mg}^{2+} \text{ is precipitated by } = 74 \text{ g Ca}(\text{OH})_2$$

$$\therefore 1272 \text{ g of } \text{Mg}^{2+} \text{ is precipitated by } = \frac{74 \times 1272}{24} \text{ g}$$

$$= 3922 \text{ g}$$

$$= 3.922 \text{ kg}$$

## Exercise 2

## Only One Option Correct

- |          |          |          |          |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 1. (b)   | 2. (b)   | 3. (c)   | 4. (b)   | 5. (c)   | 6. (c)   | 7. (b)   | 8. (a)   | 9. (c)   | 10. (b)  |
| 11. (c)  | 12. (a)  | 13. (a)  | 14. (a)  | 15. (b)  | 16. (a)  | 17. (b)  | 18. (d)  | 19. (a)  | 20. (d)  |
| 21. (b)  | 22. (b)  | 23. (d)  | 24. (c)  | 25. (d)  | 26. (c)  | 27. (b)  | 28. (d)  | 29. (c)  | 30. (a)  |
| 31. (c)  | 32. (d)  | 33. (b)  | 34. (d)  | 35. (c)  | 36. (d)  | 37. (c)  | 38. (d)  | 39. (b)  | 40. (c)  |
| 41. (a)  | 42. (b)  | 43. (a)  | 44. (c)  | 45. (b)  | 46. (c)  | 47. (b)  | 48. (b)  | 49. (c)  | 50. (b)  |
| 51. (a)  | 52. (d)  | 53. (b)  | 54. (d)  | 55. (a)  | 56. (d)  | 57. (c)  | 58. (d)  | 59. (a)  | 60. (d)  |
| 61. (c)  | 62. (d)  | 63. (d)  | 64. (d)  | 65. (b)  | 66. (d)  | 67. (c)  | 68. (b)  | 69. (a)  | 70. (a)  |
| 71. (a)  | 72. (b)  | 73. (a)  | 74. (b)  | 75. (a)  | 76. (b)  | 77. (d)  | 78. (a)  | 79. (a)  | 80. (c)  |
| 81. (c)  | 82. (b)  | 83. (d)  | 84. (c)  | 85. (c)  | 86. (a)  | 87. (a)  | 88. (b)  | 89. (d)  | 90. (c)  |
| 91. (d)  | 92. (c)  | 93. (d)  | 94. (d)  | 95. (a)  | 96. (a)  | 97. (b)  | 98. (c)  | 99. (d)  | 100. (b) |
| 101. (b) | 102. (c) | 103. (c) | 104. (a) | 105. (b) | 106. (c) | 107. (c) | 108. (a) | 109. (d) | 110. (b) |
| 111. (c) | 112. (c) | 113. (d) | 114. (a) | 115. (b) | 116. (b) | 117. (c) | 118. (b) | 119. (a) | 120. (c) |
| 121. (a) | 122. (c) | 123. (b) | 124. (b) | 125. (d) | 126. (d) | 127. (c) | 128. (b) | 129. (a) | 130. (c) |
| 131. (a) | 132. (c) | 133. (b) | 134. (b) | 135. (c) | 136. (d) | 137. (d) | 138. (b) | 139. (d) | 140. (d) |
| 141. (a) | 142. (b) | 143. (b) | 144. (a) | 145. (a) | 146. (c) | 147. (b) | 148. (b) | 149. (c) | 150. (b) |
| 151. (a) | 152. (d) | 153. (d) | 154. (c) | 155. (d) | 156. (a) | 157. (b) | 158. (c) | 159. (d) | 160. (d) |
| 161. (b) | 162. (b) | 163. (d) | 164. (a) | 165. (a) | 166. (c) | 167. (a) | 168. (c) | 169. (b) | 170. (c) |
| 171. (b) | 172. (c) | 173. (d) | 174. (c) | 175. (a) | 176. (b) | 177. (d) | 178. (d) | 179. (a) | 180. (c) |
| 181. (c) | 182. (c) | 183. (b) | 184. (b) | 185. (d) |          |          |          |          |          |

## One or More Than One Options Correct

1. (a,b,c,d)    2. (c)    3. (a,c,d)    4. (a,b)    5. (d)  
6. (c)    7. (a,b,c)    8. (d)    9. (a)    10. (a,c,d)

## Brain Twisters



$$E^\circ = E^\circ_{\text{Fe}/\text{Fe}^{2+}} + E^\circ_{\text{Cu}^{2+}/\text{Cu}}$$

$$= 0.44 + 0.34 = 0.78 \text{ V}$$

This reaction (a) is spontaneous



$$E^\circ = E^\circ_{\text{Ag}/\text{Ag}^+} + E^\circ_{\text{Cu}^{2+}/\text{Cu}}$$

$$= -0.80 + 0.34$$

$$= -0.46 \text{ V}$$

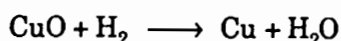
This reaction (b) is not spontaneous.



$$\Delta G^\circ = \Delta G_f^\circ(\text{CO}) - \Delta G_f^\circ(\text{CuO})$$

$$= -137.2 + 129.7$$

$$= -7.5 \text{ kJ}$$

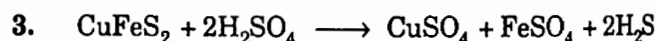


$$\Delta G^\circ = \Delta G_f^\circ(\text{H}_2\text{O}) - \Delta G_f^\circ(\text{CuO})$$

$$= -237.2 + 129.7$$

$$= -107.5 \text{ kJ}$$

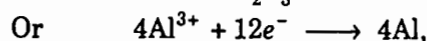
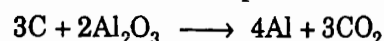
More negative value of  $\Delta G^\circ$  for reaction (II) indicates that  $\text{H}_2$  is better reducing agent.



(a)  $\text{Fe}^{2+} \equiv \text{MnO}_4^-$   
 $10 \text{ mL of Fe}^{2+} \equiv 10 \text{ mL of } 0.02 \text{ M MnO}_4^-$   
 $\equiv 10 \text{ mL of } 0.1 \text{ N MnO}_4^-$   
 $\therefore \text{Fe}^{2+} = 0.1 \text{ N}$   
 $= 5.6 \text{ g L}^{-1} \text{ in } 10 \text{ g L}^{-1} \text{ mineral}$   
 $= 56\% \text{ Fe}$

(b)  $2\text{CuSO}_4 + 4\text{KI} \longrightarrow \text{Cu}_2\text{I}_2 \downarrow + 2\text{K}_2\text{SO}_4 + \text{I}_2$   
 $\text{I}_2 \equiv \text{Na}_2\text{S}_2\text{O}_3$   
 $\therefore \text{Cu}^{2+} \equiv \text{Na}_2\text{S}_2\text{O}_3$   
 $10 \text{ mL of Cu}^{2+} \equiv 10 \text{ mL of } 0.02 \text{ M Na}_2\text{S}_2\text{O}_3$   
 $\equiv 10 \text{ mL of } 0.02 \text{ N Na}_2\text{S}_2\text{O}_3$   
 $\therefore \text{Cu}^{2+} = 0.02 \text{ N}$   
 $= 1.27 \text{ g L}^{-1} \text{ in } 10 \text{ g L}^{-1} \text{ mineral}$   
 $= 12.7\% \text{ Cu}$

4. Net reaction in Hall-Heroult process is



Number of electrons ( $n$ ) = 12

$$\Delta G^\circ = 3\Delta G_f^\circ(\text{CO}_2) - 2\Delta G_f^\circ(\text{Al}_2\text{O}_3)$$

$$= -3 \times 394 - 2(-1520)$$

$$= 1858 \text{ kJ}$$

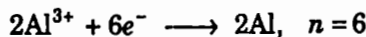
$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$

$$-E_{\text{cell}}^\circ = \frac{\Delta G^\circ}{nF} = \frac{1858 \times 1000}{12 \times 96500}$$

$$= 1.60 \text{ V}$$

For the reaction  $\text{Al}_2\text{O}_3 \longrightarrow 2\text{Al} + 3\text{O}_2$

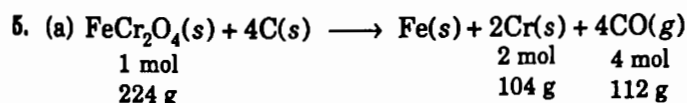
$$\Delta G^\circ = 1520 \text{ kJ}$$



$$\therefore -E_{\text{cell}}^\circ = \frac{\Delta G}{nF} = \frac{1520 \times 1000}{6 \times 96500}$$

$$= 2.62 \text{ V}$$

Thus, Hall-Heroult process takes place at lower voltage.



224 kg of chromite gives = 104 kg of Cr

$$\text{Thus, 236 kg of chromite gives} = \frac{104 \times 236}{224} \text{ kg of Cr}$$

$$= 109.57 \text{ kg Cr}$$

(b) 224 kg chromite gives = 112 kg CO

$$\text{Thus, 236 kg chromite gives} = \frac{112 \times 236}{224} \text{ kg CO}$$

$$= 118 \text{ kg CO}$$

$$= 4214.2857 \text{ mol}$$

Using equation  $pV = nRT$ ;  $T = 298 \text{ K}$ ,  $p = \frac{740}{760} \text{ atm}$

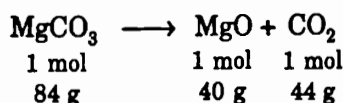
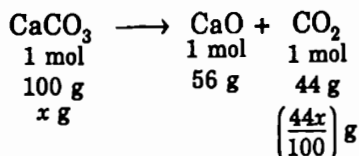
$$V = \frac{nRT}{p} = \frac{4214.2857 \times 0.0821 \times 298}{(740/760)}$$

$$= 105.892 \times 10^3 \text{ L CO}$$

6. (1) Copper (2) Platinum (3) Silver (4) Iron  
(5) Barium (6) Zinc (7) Lithium (8) Magnesium

7. Let  $\text{CaCO}_3 = x \text{ g}$

then,  $\text{MgCO}_3 = (18.4 - x) \text{ g}$



$$\therefore (18.4 - x) \text{ g} \quad \frac{44}{84} (18.4 - x) \text{ g}$$

$$\text{Total CO}_2 = \frac{44x}{100} + \frac{44(18.4 - x)}{84} = 8.8 \text{ (given)}$$

This gives  $x = 10 \text{ g}$

$$\therefore \text{CaCO}_3 = 10 \text{ g} = 0.1 \text{ mol}$$

$$\text{MgCO}_3 = 18.4 - 10 = 8.4 \text{ g} = 0.1 \text{ mol}$$

Total moles of  $\text{CaCO}_3$  and  $\text{MgCO}_3 = 0.2 \text{ mol}$

$$\therefore \text{CaCO}_3 = 50 \text{ mol}\%$$

$$\text{MgCO}_3 = 50 \text{ mol}\%$$

## Passage Comprehension Questions

### Passage 1

1. (b)    2. (c)    3. (a)    4. (c)    5. (d)

### Passage 2

$$1. \text{ (a) } \text{ZnS} = 90.6\% = \text{ZnO} \xrightarrow{100\%} \text{ZnSO}_4 \xrightarrow{98.2\%} \text{Zn}$$

1 mol ZnS gives 1 mol Zn but based on % yield, 1 mol ZnS gives =  $0.906 \times 1.0 \times 0.982$

$$= 0.8897 \text{ mol Zn}$$

$$225 \text{ kg ZnS} = \frac{225}{97} \text{ kmol ZnS} = 2.32 \text{ kmol ZnS}$$

$$= 2.06 \text{ kilomol Zn}$$

$$= 134 \text{ kg Zn}$$

2. (d)

$$w = zit$$

$$i = \frac{w}{zt}$$

$$= \frac{134 \times 10^3 \text{ g}}{\left(\frac{65}{2 \times 96500}\right) (30 \times 24 \times 60 \times 60)}$$

$$= 154 \text{ A}$$

where,

$z$  = electrochemical equivalent

$$= \left( \frac{\text{atomic mass}}{\text{electrons} \times 96500} \right)$$

= time in seconds

3. (b)



5. (a) 98%  $\text{H}_2\text{SO}_4$  by weight  $\text{H}_2\text{SO}_4$  ( $d = 1.8 \text{ g/mL}$ ) is 18 M

$$100 \text{ g H}_2\text{SO}_4 \text{ solution has} = 98 \text{ g H}_2\text{SO}_4$$

$$\frac{100}{1.8} \text{ mL H}_2\text{SO}_4 \text{ solution has} = 98 \text{ g H}_2\text{SO}_4$$

$$\text{molarity} = \frac{\text{mol}}{\text{litre}} = \frac{(98/98)}{\frac{100}{1.8 \times 1000}}$$

$$= 18 \text{ M}$$

$\text{ZnO} = 2.32 \text{ kilomol}$  in step (i) assuming 100% yield

$$\text{H}_2\text{SO}_4 = 2.32 \times 10^3 \text{ mol}$$

$$18 \text{ mol H}_2\text{SO}_4 \text{ are in} = 1 \text{ L}$$

$$\therefore 2.32 \times 10^3 \text{ mol are in} = 129 \text{ mol}$$

$$\approx 130$$

**Passage 3**

1. (b) 2. (d)

**Passage 4**

1. (a) 2. (b) 3. (a)

**Passage 5**

1. (b) 2. (a) 3. (c) 4. (d)

**Passage 6**

1. (d) 2. (b) 3. (c) 4. (a) 5. (b)

**Passage 7**

1. (a) 2. (c)

3. (b)
- $w = zit$
- $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$

$$\text{Equivalent weight} = \frac{63.5}{2}$$

$$\text{where } z = \frac{\text{electrochemical equivalent}}{\text{equivalent weight}} = \frac{63.5}{96500}$$

$$i = \text{current (A)}$$

$$t = \text{time (s)}$$

$$65.6 = \frac{63.5 \times 50 \times t}{2 \times 96500}$$

$$t = \frac{2 \times 96500 \times 65.6}{63.5 \times 50} \text{ s}$$

$$= 1.1 \text{ h}$$

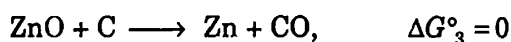
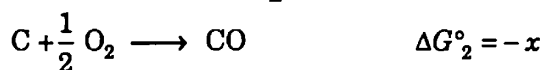
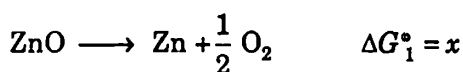
**Passage 8**

1. (c) 2. (a) 3. (d) 4. (b,c) 5. (a)

**Passage 9**

1. (a)

2. (c)



System is at equilibrium;

$\Delta G_1^\circ = -\Delta G_2^\circ$  since zinc and carbon have equal affinity for oxygen.

3. (b) This will be above a temperature when two curves intersect.
4. (d)  $\Delta G^\circ = \text{most negative.}$

**Passage 10**

1. (a) 2. (c) 3. (a,b) 4. (d) 5. (a,c)
6. (c)

**Passage 11**

1. (c),  $\Delta G^\circ$  being more negative 2. (d) 3. (a,c)

**Assertion & Reason**

1. (b) 2. (a) 3. (e) 4. (b) 5. (a) 6. (b)

**True & False**

1. F 2. T 3. T 4. F 5. T 6. F
7. T 8. T 9. F 10. F 11. F 12. T
13. F 14. T 15. T 16. F 17. F 18. T
19. T 20. F

**Fill in the Blanks**

1.  $\text{Cr}_2\text{O}_3$ ,  $\text{N}_2$  2. Al 3.  $[\text{Ag}(\text{CN})_2]^-$  4. higher
5. Wrought 6. Pig 7. oxygen 8. aluminium
9. Frasch process 10. van Arkel-de-Boer process
11. Kroll process 12. copper 13. magnesium
14.  $\text{AlN}$ ,  $\text{Al}(\text{OH})_3$  15. Hall-Heroult process, lower, increase
16. silver 17. methanides, methane 18. haemoglobin
19. ferrochrome 20. fool's gold 21. 75% 22. steel
23. pig, wrought 24. steel 25. steel 26. nickel
27. chalcocite 28.  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  29. Parke's
30. an insecticide

**Matrix-Match Type Questions****I. Only One Correct**

1. (A)—(4); (B)—(1); (C)—(2); (D)—(3)
2. (A)—(2); (B)—(4); (C)—(3); (D)—(1)
3. (A)—(4); (B)—(1); (C)—(2); (D)—(3)
4. (A)—(3); (B)—(1); (C)—(2); (D)—(4)
5. (A)—(3); (B)—(4); (C)—(2); (D)—(1)
6. (A)—(3); (B)—(5); (C)—(1); (D)—(2)
- (E)—(4)

**II. One or More Correct**

1. (A)—(1,6); (B)—(6); (C)—(1,2,3,6); (D)—(1,5) (E)—(4,5)
2. (A)—(3,4,6,7); (B)—(1,2,4); (C)—(4,5,7); (D)—(2,5) (E)—(1,6)

**Integer Answer Types****Set I**

|             |   |   |   |   |   |   |   |   |
|-------------|---|---|---|---|---|---|---|---|
| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Answers →   | 2 | 7 | 2 | 6 | 3 | 4 | 3 | 1 |
|             | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
|             | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|             | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
|             | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
|             | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
|             | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
|             | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
|             | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
|             | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
|             | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |

## Set II

Questions →  
Answers →

|   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 4 | 2 | 7 | 6 | 9 | 9 | 2 | 9 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
| 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
| 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
| 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |

## Test Yourself on the Periodic Table

## 1. Minerals are

**A: Sulphide      B: Carbonate      C: Chloride      D: Oxide**

**E : Sulphide      F : Uncombined form**

The grid-in response area consists of two rows of bubbles. The top row has 10 bubbles, and the bottom row has 10 bubbles. The following table shows the state of each bubble:

| Bubble | Top Row | Bottom Row |
|--------|---------|------------|
| 1      |         |            |
| 2      |         |            |
| 3      | C       |            |
| 4      | B       |            |
| 5      |         |            |
| 6      | D       |            |
| 7      |         |            |
| 8      |         |            |
| 9      | A       |            |
| 10     |         |            |
| 11     | F       |            |
| 12     | E       |            |
| 13     |         |            |
| 14     |         |            |
| 15     |         |            |
| 16     |         |            |
| 17     |         |            |
| 18     |         |            |
| 19     |         |            |
| 20     |         |            |

2. A (Mg) : Electrolysis of molten  $\text{MgCl}_2$   
 B (Al) : Electrolytic reduction of  $(\text{Al}_2\text{O}_3 + \text{Na}_3\text{AlF}_6)$   
 C (Au) : Cyanide reduction process  

$$2 [\text{Au}(\text{CN})_2]^- + \text{Zn} \longrightarrow [\text{Zn}(\text{CN})_4]^{2-} + 2\text{Au} \downarrow$$
  
 D (Cu) : Bessemerisation followed by electrolysis of aq.  $\text{CuSO}_4$  solution using impure Cu as anode  
 E (Sn) : Reduction of  $\text{SnO}_2$  by charcoal



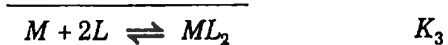
# Coordination Compounds

"Even when, to judge by the valence number, the combining power of certain atoms is exhausted, they still possess in most cases, the power of participating further in the construction of complex molecules with the formation of very definite linkages. The possibility of this action is to be traced back to the fact that, besides the affinity bonds designated as principal valences, still other bonds called auxiliary valences, may be called into action."

Alfred Werner

## Quick Points

- For the stepwise formation of  $ML_2$  from  $M$  and  $L$



$$K_3 = K_1 K_2$$

$$\log K_3 = \log K_1 + \log K_2$$

$$pK_3 = pK_1 + pK_2$$

- $O_2^-$  is called superoxide ion.
- Anions outside coordination sphere ionise, greater the number of ions larger the conductance



- van't Hoff factor  $i$

$$i = [1 + (y - 1)x]$$

where,  $y$  = number of ions per unit of the complex/species

$x$  = degree of ionisation

$i = (1 + 3x)$  in the above case since,  $y = 4$

- Electron-pair donor is a Lewis base and electron-pair acceptor is a Lewis acid.

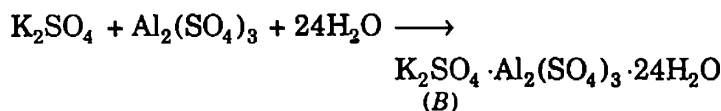
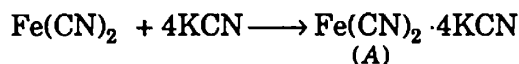
## Learning Framework of the Chapter

- Double Salts and Coordination Compounds
- Ligands
- Coordination Number
- Nomenclature
- Effective Atomic Number
- Isomerism in Complexes
- Werner Theory of Coordination Compounds
- Bonding in Complexes
- Stability Constants and Stability of Coordination Compounds
- Applications of Coordination Chemistry



## Double Salts and Coordination Compounds

- When  $\text{Fe}(\text{CN})_2$  solution is treated with KCN solution, species formed, no longer, gives tests of  $\text{Fe}^{2+}$  and  $\text{CN}^-$ .
- When  $\text{K}_2\text{SO}_4$  solution is treated with  $\text{Al}_2(\text{SO}_4)_3$  solution, species formed gives tests of  $\text{K}^+$ ,  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$ .



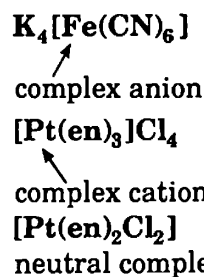
We call them addition compounds of

**Type I :** those which lose their identity in solution (double salt) as alum (B).

**Type II :** those which retain their identity in solution (complexes) as potassium ferrocyanide (A).

Most *d*-transition metal ions have vacant *d*-orbitals that can accommodate electron pairs. Many act as Lewis acids by forming coordinate covalent bonds in **coordination compounds (coordination complexes or complex ions)**.

A complex ion is a metal ion with Lewis bases (ligand) attached to it through coordinate covalent bonds (also called coordination). A complex (or coordination compound) is a compound consisting either of complex ions with other ions of opposite charge.



$\text{K}^+$  is other ion

$\text{Cl}^-$  is other ion

Many important biological substances are coordination compounds. Haemoglobin and chlorophyll are two such examples. Haemoglobin is a protein that carries  $\text{O}_2$  in blood. It contains iron (II) ions bound to large porphyrin rings. Chlorophyll is necessary for photosynthesis in plants. It contains magnesium ions bound to porphyrin rings. Vitamin B-12 is a large complex of cobalt.

## Ligands

A ligand is a species that is capable of donating an electron pair(s) to a central metal or metal ion. It is a **Lewis base**. In accepting electron pairs, the central ion acts as a **Lewis acid**.

- Ligand is said to be **unidentate** if it has only one pair of electrons that it can donate (Table 18.1).
- Ligand is said to be **bidentate**, **tridentate**, **tetradentate** etc. depending on the number of electron-pairs that it can donate. (Table 18.2).

Table 18.1 Some Common Unidentate Ligands

| Neutral                               |                     | Anions (replacing ide by o)       |                | Anions (replacing e by o)    |                 |
|---------------------------------------|---------------------|-----------------------------------|----------------|------------------------------|-----------------|
| Formula                               | Name as ligand      | Formula                           | Name as ligand | Formula                      | Name as ligand  |
| <u>O</u> $\text{H}_2$                 | aqua                | <u>F</u> $^-$ (fluoride)          | fluoro         | <u>S</u> $\text{O}_4^{2-}$   | sulphato        |
| <u>N</u> $\text{H}_3$                 | ammine              | <u>Cl</u> $^-$                    | chloro         | <u>S</u> $_2\text{O}_3^{2-}$ | thiosulphato    |
| <u>C</u> $\text{O}$                   | carbonyl            | <u>Br</u> $^-$                    | bromo          | <u>C</u> $\text{O}_3^{2-}$   | carbonato       |
| <u>N</u> $\text{O}$                   | nitrosyl            | <u>I</u> $^-$                     | iodo           | <u>N</u> $\text{O}_2$        | nitro*          |
| <u>N</u> $\text{H}_2\text{CH}_3$      | methylamine         | <u>O</u> $^{2-}$ (oxide)          | oxo            | <u>O</u> $\text{NO}^-$       | nitrito*        |
| <u>N</u> $\text{C}_5\text{H}_5$ or Py | pyridine            | <u>O</u> $\text{H}^-$ (hydroxide) | hydroxo        | <u>S</u> $\text{CN}^-$       | thiocyanato*    |
| <u>N</u> $(\text{C}_2\text{H}_5)_3$   | triethylamine       | <u>CN</u> $^-$ (cyanide)          | cyano*         | <u>N</u> $\text{CS}^-$       | isothiocyanato* |
| <u>N</u> $(\text{CH}_3)_3$            | trimethylamine      | <u>N</u> $\text{C}$               | isocyano*      |                              |                 |
| <u>P</u> $(\text{C}_6\text{H}_5)_3$   | triphenyl phosphine | <u>S</u> $^{2-}$                  | sulphido       |                              |                 |
| <u>P</u> $\text{H}_3$                 | phosphine           | <u>H</u> $^-$                     | hydrido        |                              |                 |

\* underlined atoms are electron-donating, ambidentate.

Table 18.2 Some Common Multidentate Ligands (Chelating Agents)

| Abbreviation | Multi       | Name                             | Formula                                                                                                                                                                                                                                                                                          | Charge |
|--------------|-------------|----------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------|
| en           | bidentate   | ethylenediamine                  | $\begin{array}{c} \text{CH}_2\text{NH}_2 \\   \\ \text{CH}_2\text{NH}_2 \end{array}$                                                                                                                                                                                                             | 0      |
| ox           | bidentate   | oxalate ion                      | $\begin{array}{c} \text{COO}^- \\   \\ \text{COO}^- \end{array}$                                                                                                                                                                                                                                 | -2     |
| gly          | bidentate   | glycinate ion                    | $\begin{array}{c} \text{CH}_2\text{NH}_2 \\   \\ \text{COO}^- \end{array}$                                                                                                                                                                                                                       | -1     |
| DMG          | bidentate   | dimethylglyoximate ion           | $\begin{array}{c} \text{CH}_3-\text{C}=\text{NO}^- \\   \\ \text{CH}_3-\text{C}=\text{NOH} \end{array}$                                                                                                                                                                                          | -1     |
| dien         | tridentate  | diethylene-triamine              | $\text{H}_2\text{N}(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2\text{NH}_2$                                                                                                                                                                                                                         | 0      |
| EDTA         | hexadentate | ethylenediamine tetraacetate ion | $\left[ \begin{array}{c} ^-\text{OOCCH}_2 \\ \diagup \quad \diagdown \\ \text{N}-\text{CH}_2-\text{CH}_2-\text{N} \\ \diagdown \quad \diagup \\ ^-\text{OOCCH}_2 \end{array} \begin{array}{c} \text{CH}_2\text{COO}^- \\ \diagup \quad \diagdown \\ \text{CH}_2\text{COO}^- \end{array} \right]$ | -4     |

(a)  $\text{:NH}_3$ , one electron-pair available for donation—unidentate.

(b)  $\begin{array}{c} \text{CH}_2\text{NH}_2 \\ | \\ \text{CH}_2\text{NH}_2 \end{array}$ , two electron-pairs available for donation—bidentate.

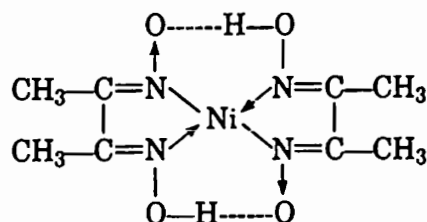
- Some ligands can be coordinated to the metal or metal ion through either of the sides. They are called “ambidentate” ligands.

If the nitrite ion is attached through N atom ( $-\text{NO}_2$ ), it is nitro; if attached through O atom ( $-\text{ONO}$ ), then nitrito.

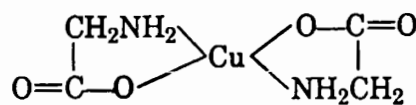
- Ligands can be
  - neutral molecules such as  $\text{H}_2\text{O}$
  - anions such as  $\text{CN}^-$ ,  $\text{C}_2\text{O}_4^{2-}$
  - cations [but in rare cases since an electron pair on a cation is held firmly by the positive charge and would not be involved in coordinate bonding.]
- Ligands forming complex with metal do not ionise.
- In some cases it is not possible to identify donor atoms, because the bonding electrons are not localised on specific atoms. Ethylene ( $\text{CH}_2=\text{CH}_2$ ) bonds to transition metal through the electrons in their double bonds.

### DEEP Focus

These are called **multidentate ligands** (Table 18.2). When the bonding of a multidentate ligand to a metal ion produces a ring (usually five- or six-membered), we refer to the complex as a **chelate** (pronounced-keylate). The multidentate ligand is called a **chelating agent** and the process of chelate formation is called **chelation**. The number of such ligating groups indicate the denticity (unidentate, bidentate ..... ) of the ligand.



nickel (II) dimethyl glyoximate (chelate)  
[bis-(dimethylglyoximate) nickel (II)]



copper (II) glycinate (chelate)  
[trans-bisglycinato copper (II)]

### Coordination Number

The coordination number (C.N.) of a metal atom in a complex is the total number of bonds the metal atom forms with ligands. Some common coordination numbers of metal ions are summarised in Table 18.3.

### Chelates

Some ligands are capable of donating more than a single electron pair, from different atoms in the ligand and to different sites in the geometric structure of a complex.

Table 18.3 Coordination Number (C.N.) of Metal Ions

| Metal ion                           | C.N. |
|-------------------------------------|------|
| Ag <sup>+</sup>                     | 2    |
| Cu <sup>+</sup>                     | 2, 4 |
| Cu <sup>2+</sup>                    | 4, 6 |
| Au <sup>+</sup>                     | 2, 6 |
| Ca <sup>2+</sup>                    | 6    |
| Fe <sup>2+</sup> , Fe <sup>3+</sup> | 6    |
| Co <sup>2+</sup>                    | 4, 6 |
| Co <sup>3+</sup>                    | 6    |
| Ni <sup>2+</sup>                    | 4, 6 |
| Zn <sup>2+</sup>                    | 4    |
| Al <sup>3+</sup>                    | 4, 6 |
| Sc <sup>3+</sup>                    | 6    |
| Cr <sup>3+</sup>                    | 6    |
| Pt <sup>2+</sup>                    | 4    |
| Pt <sup>4+</sup>                    | 6    |

Examples of complexes of various C.N. are given in Table 18.4.

Table 18.4 Examples of Complexes of Various Coordination Numbers

| Complex                                                                 | C.N. |
|-------------------------------------------------------------------------|------|
| [Ag(NH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>                       | 2    |
| [HgI <sub>3</sub> ] <sup>-</sup>                                        | 3    |
| PtCl <sub>4</sub> <sup>2-</sup> , Ni(CO) <sub>4</sub>                   | 4    |
| Fe(CO) <sub>5</sub> , [Co(CN) <sub>5</sub> ] <sup>3-</sup>              | 5    |
| [Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> , W(CO) <sub>6</sub> | 6    |
| [Mo(CN) <sub>7</sub> ] <sup>3-</sup>                                    | 7    |
| [W(CN) <sub>8</sub> ] <sup>4-</sup>                                     | 8    |

## Nomenclature

The definite source for the naming of inorganic compounds is **Nomenclature of Inorganic Compounds 2005** (N.G. Connelly and T. Damhus, Sr. Eds. Royal Society of Chemistry 2005)

Following rules are adopted for naming a complex ion;

- Cations are named before anions
- Oxidation state (O.S.) of the central metal ion is denoted by Roman numeral.

|                   | Cation      | O.S. anion |
|-------------------|-------------|------------|
| CuCl              | Copper (I)  | chloride   |
| CuCl <sub>2</sub> | Copper (II) | chloride   |
| FeCl <sub>2</sub> | Iron (II)   | chloride   |
| FeCl <sub>3</sub> | Iron (III)  | chloride   |

- The names of ligands are given first followed by the name of the central metal ion.
- The names of ligands that are anions and ending with

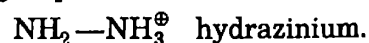
'ide' are changed to 'o'

'ite' are changed to 'ito'

'ate' are changed to 'ato' (Table 18.1 and 18.2)

- Many ligands that are molecules carry the unmodified name (Table 18.1 and 18.2)

- Positive groups end in -ium



### DEEP Focus

- When there are several ligands of the same kind, we normally use the prefixes **di**, **tri**, **tetra**, **penta** and **hexa** to show the number of ligands of that type. An exception occurs when the name of the ligands includes a number, for example as in ethylenediamine (en). To avoid confusion in such cases, **bis**, **tris** and **tetrakis** are used instead of di, tri, and tetra, and the name of the ligand is placed in brackets.

bis (ethylenediamine)

- If anion is a complex, then metal ends with 'ate'

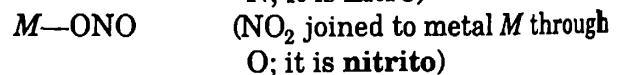
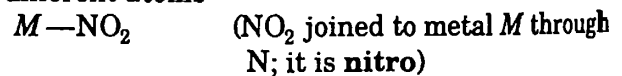


tetracyanonickelate (II) ion

|           |                    |
|-----------|--------------------|
| lead      | — <b>plumbate</b>  |
| gold      | — <b>aurate</b>    |
| zinc      | — <b>zincate</b>   |
| tin       | — <b>stannate</b>  |
| silver    | — <b>argentate</b> |
| cobalt    | — <b>cobaltate</b> |
| iron      | — <b>ferrate</b>   |
| aluminium | — <b>aluminate</b> |
| manganese | — <b>manganate</b> |
| copper    | — <b>cuprate</b>   |
| chromium  | — <b>chromate</b>  |
| platinum  | — <b>platinate</b> |

- If the complex contains two or more metal atoms, it is termed polynuclear. The bridging ligands which link the two metal atoms together are indicated by the prefix  $\mu$  —.

- Ambidentate ligands may be attached through different atoms



Similarly, the SCN group may bond  $M-\text{SCN}$  (thiocyanato) or  $M-\text{NCS}$  (isothiocyanato). They may be named

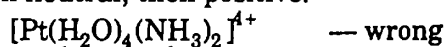
thiocyanato-S [to indicate S coordinated to metal  $M$ ]

thiocyanato-N [to indicate N coordinated to metal  $M$ ]

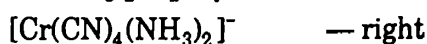
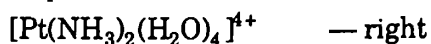
- When writing (not naming) the formula of the complex :

- complex ion should be enclosed by square brackets and

- ligands are placed after metal in the alphabetical order but first negative ligands, then neutral, then positive.

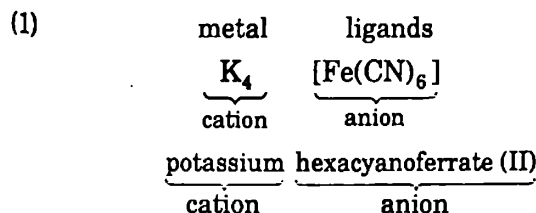


aqua      ammine

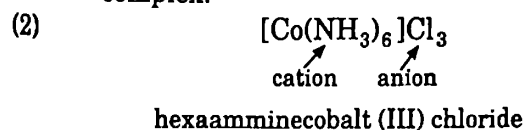


negative      neutral

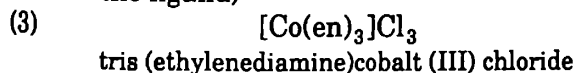
### Examples



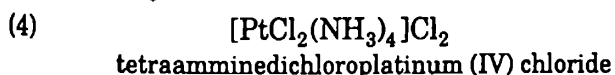
- anion is a complex hence its metal ends with **ate** (ferrate),
- ligands are named before metal ion of the complex.



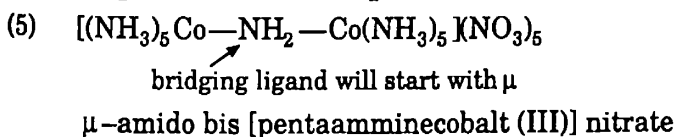
- cation is a complex
- anion will not change its name (since it is not the ligand)



- tris is used to indicate three ligands **en** (ethylenediamine) since it also carries **di**.



- $\text{NH}_3$  (ammine) and  $\text{Cl}$  (chloro) are two types of ligands **named in alphabetical order**:



### 1. In the following examples, **complex ion** exists as **cation**:

- (a)  $[\text{Fe}(\text{NH}_3)_6]\text{Cl}_3$   
Hexaammineiron (III) chloride
- (b)  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$   
Pentaamminechlorocobalt (III) ion
- (c)  $[\text{Co}(\text{SO}_4)(\text{NH}_3)_4][\text{NO}_3]$   
Tetraamminesulphatocobalt (III) nitrate
- (d)  $[\text{Co}(\text{Cl})(\text{NO}_2)(\text{NH}_3)_4]^+$   
Tetraamminechloronitrocobalt (III) ion

### 2. In the following examples, **complex ion** exists as **anion**

- (a)  $[\text{ZnCl}_4]^{2-}$   
Tetrachlorozincate (II) ion
- (b)  $[\text{AlH}_4]^-$   
Tetrahydridoaluminate (III) ion

- (c)  $\text{K}_4[\text{Fe}(\text{CN})_6]$   
Potassium hexacyanoferrate (II)
- (d)  $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$   
Sodium dithiosulphatoargenate (I)
- (e)  $\text{Na}_2[\text{OsCl}_5\text{N}]$   
Sodium pentachloronitridoosmate (VI)
- (f)  $\text{K}_2[\text{PtCl}_6]$   
Potassium hexachloroplatinate (IV)
- (g)  $\text{K}_2[\text{Cr}(\text{CN})_2(\text{O}_2)_2(\text{O}_2)\text{NH}_3]$   
Potassium amminedicyanodioxoperoxo chromate (VI)
- (h)  $[\text{Zn}(\text{NCS})_4]^{2-}$   
Tetrathiocyanato-N-zincate (II) ion  
(N indicates that ligand joined to metal ion through N-side)

### 3. In the following examples, **organic ligands** have been used :

- (a)  $[\text{Pt}(\text{Py})_2][\text{PtCl}_4]$   
Tetrapyridineplatinum (II)  
tetrachloroplatinate (II)
- (b)  $[\text{Cr}(\text{en})_3]\text{Cl}_3$   
di- or -tris (ethylenediamine) chromium (III) chloride
- (c)  $[\text{Pt}(\text{en})_2]^{2+}$   
Bis (ethylenediamine) Platinum (II) ion
- (d)  $[\text{Cr}(\text{C}_6\text{H}_6)_2]$   
Bis (benzene) chromium (0)
- (e)  $[\text{Fe}(\text{C}_5\text{H}_5)_2]$   
Bis (cyclopentadienyl) iron (II)

### 4. In the following examples, **bridging groups** have been used:

- (a) 
$$\left[ (\text{en})_2\text{Co} \begin{array}{c} \diagup \text{NH} \diagdown \\ \diagdown \text{OH} \diagup \end{array} \text{Co}(\text{en})_2 \right]^{4+}$$
  
Tetrakis(ethylenediamine)- $\mu$ -hydroxo- $\mu$ -imidodicobalt (III) ion.
- (b)  $[(\text{CO})_3\text{Fe}(\text{CO})_3\text{Fe}(\text{CO})_3]$   
Tri- $\mu$ -carbonyl-bis (tricarbonyliron (0))
- (c) 
$$\begin{array}{c} (\text{C}_6\text{H}_5)_3\text{P} \quad \text{Cl} \quad \text{Cl} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{Pd} \quad \text{---} \quad \text{Pd} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{Cl} \quad \text{Cl} \quad \text{P}(\text{C}_6\text{H}_5)_3 \end{array}$$
  
(.... line used to indicate symmetry)  
Trans-bis(chlorotriphenylphosphine)- $\mu$ -chloropalladium(I)  
or  
Chlorotriphenylphosphine palladium (II)  
 $\mu$ -dichlorochlorotriphenylphosphine palladium (II)

## Effective Atomic Number

Each ligand donates an electron pair to the metal ion, thus forming a coordinate bond. Transition metals form coordination compounds very readily because they have vacant *d*-orbitals which can accommodate these electron pairs. Metal ion in the complex tends to attain

nearest stable inert gas configuration by gaining electrons from ligands. **Effective atomic number (EAN)** of the metal in a complex is given by

$$\text{EAN} = Z - (\text{O.N.}) + 2(\text{C.N.})$$

EAN of some metals in complexes is summarised in Table 18.5.

Table 18.5 Effective Atomic Numbers of Some Metal in Complexes

| Atom | Atomic number (Z) | Complex                                                       | C.N. | Electrons lost in ion formation (O.N.) | Electrons gained by coordination | EAN    |
|------|-------------------|---------------------------------------------------------------|------|----------------------------------------|----------------------------------|--------|
| Cr   | 24                | $[\text{Cr}(\text{CO})_6]$                                    | 6    | 0                                      | 12                               | 36     |
| Ni   | 28                | $\text{Ni}(\text{CO})_4$                                      | 4    | 0                                      | 8                                | 36     |
| Fe   | 26                | $[\text{Fe}(\text{CN})_6]^{4-}$                               | 6    | 2                                      | 12                               | 36     |
| Fe   | 26                | $[\text{Fe}(\text{NH}_3)_6]^{2+}$                             | 6    | 2                                      | 12                               | 36     |
| Cu   | 29                | $[\text{Cu}(\text{CN})_4]^{3-}$                               | 4    | 1                                      | 8                                | 36     |
| Co   | 27                | $[\text{Co}(\text{en})_3]^{3+}$ , (en) is bidentate           | 6    | 3                                      | 12                               | 36     |
| Pd   | 46                | $[\text{Pd}(\text{H}_2\text{O})_6]^{4+}$                      | 6    | 4                                      | 12                               | 54[Xe] |
| Pt   | 78                | $[\text{PtCl}_6]^{2-}$                                        | 6    | 4                                      | 12                               | 86[Rn] |
| Fe   | 26                | $[\text{Fe}(\text{CN})_6]^{3-}$                               | 6    | 3                                      | 12                               | 35     |
| Ag   | 47                | $[\text{Ag}(\text{CN})_2]^-$                                  | 2    | 1                                      | 4                                | 50     |
| Al   | 13                | $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$ , ox is bidentate. | 6    | 3                                      | 12                               | 22     |

(where O.N. is oxidation number, C.N. the coordination number and Z the atomic number).

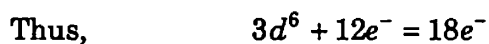
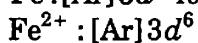
EAN can also be given by

$$\text{EAN} = Z - (\text{O.N.}) + 2(\text{Ligands})$$

assuming that each ligand is unidentate.

## 18-Electrons System

If there are total of 18-electrons attained due to gain of coordination electrons of ligands including  $(n-1)d^xns^y$  electrons of metal/metal ion, the complex is said to attain 18-electrons configuration.



## Isomerism in Complexes

Compounds that have the same chemical formula but different structural arrangement are called **isomers**.

### A. Structural Isomerism

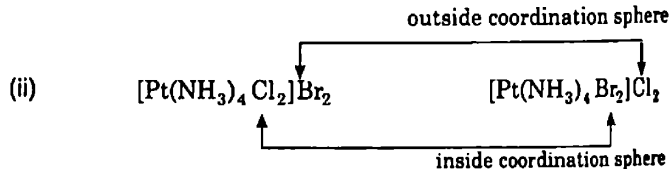
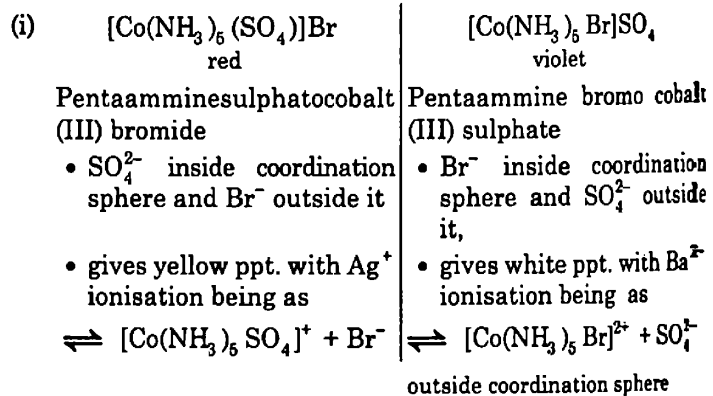
Structural isomers are isomers that differ in how the atoms are joined together—that is, in the order in which the atoms are bonded to one another.

( $\text{H}-\text{N}=\text{C}=\text{O}$  and  $\text{N}=\text{C}-\text{O}-\text{H}$  are structural isomers)

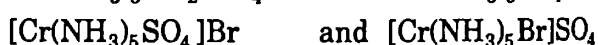
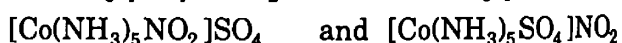
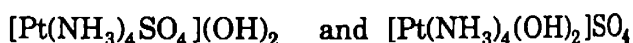
These are of the following types:

#### (a) Ionisation Isomerism

This type of isomerism occurs when there is an interchange of groups between the coordination sphere of the metal ion and the ions outside this sphere. Examples are:



Other examples are:



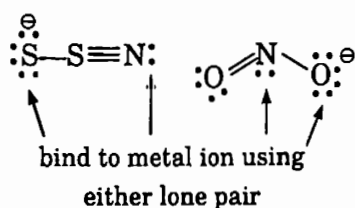
#### (b) Coordination Isomerism

When both the positive and negative ions are complex ions, isomerism may be caused by the interchange of ligands between the anion and cation. This arises only if cationic and anionic metals have same C.N. and charge. Examples are:

- same charge  
(i)  $[\text{Co}(\text{NH}_3)_6]^{3+} [\text{Cr}(\text{CN})_6]^{3-}$   
same C.N. = 6  
Hexaamminecobalt (III) hexacyanochromate (III)  
 $[\text{Cr}(\text{NH}_3)_6]^{3+} [\text{Co}(\text{CN})_6]^{3-}$   
Hexamminechromium (III) hexacyanocobaltate (III)
- (ii)  $[\text{Co}(\text{en})_3] [\text{Cr}(\text{CN})_6]$   
 $[\text{Cr}(\text{en})_3] [\text{Co}(\text{CN})_6]$
- (iii)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2] [\text{PtCl}_4]$   
 $[\text{Pt}(\text{NH}_3)_4] [\text{PtCl}_6]$

### (c) Linkage Isomerism

This type of isomerism arises when the ligand may attach to the central metal ion of a complex in different ways. (Such ligands are called **ambidentate ligands**). Nitrite ion has electron pairs available for coordination both on N and O atoms. (refer Table 18.1)



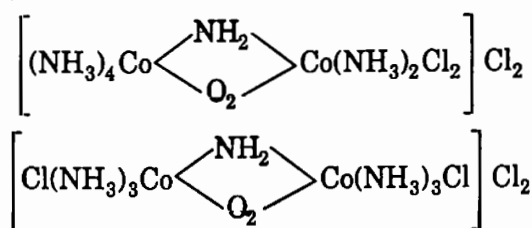
#### Examples :

- (i)  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$   
pentaamminenitritocobalt (III)      pentaamminenitrocobalt (III)  
chloride (red), decomposes in acids      chloride (yellow), stable in acids
- (ii)  $[\text{Mn}(\text{CO})_5(\text{SCN})]^+$  and  $[\text{Mn}(\text{CO})_5(\text{NCS})]^+$   
pentacarbonylthiocyanato-S-manganese (II) ion      pentacarbonylthiocyanato-N-manganese (II) ion

### (d) Coordination Position Isomerism

In polynuclear complexes an interchange of ligands between the different metal nuclei gives rise to position isomerism.

Example :

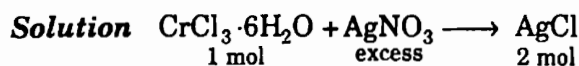


### (e) Hydrate (Solvate) Isomerism

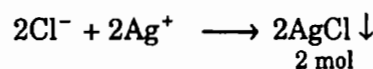
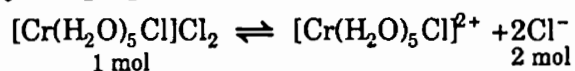
Hydrate isomers are isomers of a complex that differ in the placement of water molecules in the complex.  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  have following hydrate isomers:

- $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  — violet (anhydrous)  
 $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  — light green (monohydrate)  
 $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  — dark green (dihydrate)

**Illustration 1** One mole of the complex  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  on reaction with excess of aq.  $\text{AgNO}_3$  gives two moles of white precipitate of  $\text{AgCl}$ . What is the complex?



This reaction indicates that two Cl are outside the coordinate sphere and one Cl inside it. Coordination number of six of Cr ion is satisfied by five  $\text{H}_2\text{O}$  and one Cl as ligands. Thus, this is monohydrate complex  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$



### (f) Electronic Isomerism

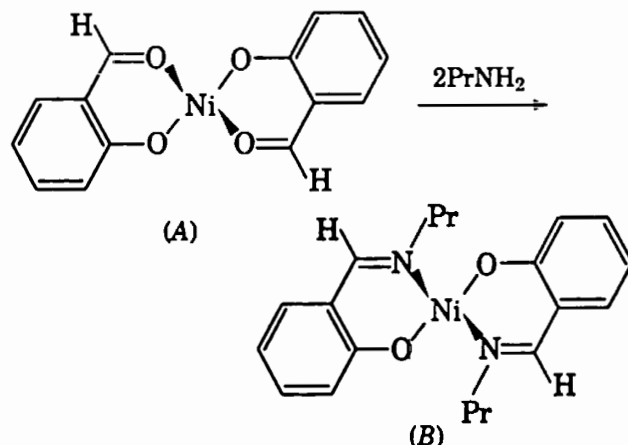
The complex  $[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$  exists in two forms. One is black paramagnetic while the other is pink and diamagnetic. Structural studies show that the black isomer is a Co(II) complex containing neutral NO group whereas the pink one is a Co(III) complex with  $\text{NO}^-$  ligand. This type of isomerism is called **electronic isomerism**.

### (g) Ligand Isomerism

Isomerism may also arise due to isomerism in the ligand set. The effect of changing an alkyl chain on a ligand from a linear to a branched structure is sufficient to induce quite profound structural changes in the complex.

Consider reaction of **A**, bis-(salicylaldehyde) nickel (II) with propyl amine to give **B**, bis-(N-propylsalicylidene aminato) nickel (II).

The use of *n*-propyl amine or isopropylamine gives two isomers in this reaction. The more sterically hindered isopropyl amine results in a complex distorted away from the square planar geometry displayed by the *n*-propyl complex towards a tetrahedral geometry.



## (h) Polymerisation Isomerism

This term is used to describe compounds having same empirical formula but different molecular compositions. The difference from normal polymerisation is that here we have differences in arrangements of group as multiplication of molecular weight. Thus, value of  $n$  in the empirical formula  $[ML_m]_n$  varies.

$[Pt(NH_3)_2Cl_2]_n$  gives

(A)  $[Pt(NH_3)_2Cl_2]$  if  $n = 1$  and

(B)  $[Pt(NH_3)_4][PtCl_4]$  if  $n = 2$

and thus (A) and (B) are polymerisation isomers,  $[Co(NH_3)_3(NO_2)_3]$  gives following isomers

| Formula                                    | Molecular weight |
|--------------------------------------------|------------------|
| $[Co(NH_3)_6][Co(NO_2)_6]$                 | double           |
| $[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$ | double           |
| $[Co(NH_3)_5(NO_2)][Co(NH_3)_2(NO_2)_4]_2$ | triple           |
| $[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$       | quadruple        |
| $[Co(NH_3)_4(NO_2)_3][Co(NO_2)_6]$         | quadruple        |
| $[Co(NH_3)_5(NO_2)]_3[Co(NO_2)_6]_2$       | quintuple        |

## B. Stereo Isomers

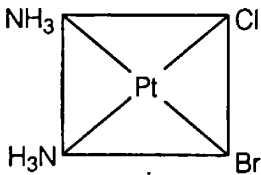
These are the isomers in which the atoms are bonded to each other in the same order but that differ in the precise arrangement of these atoms in space. These are of the following types:

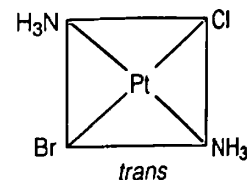
### (a) Geometric Isomerism

Geometric isomers are isomers in which the atoms are joined to one another in the same way but that differ because some atoms occupy different relative positions in space.

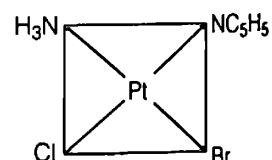
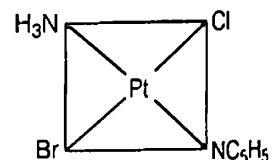
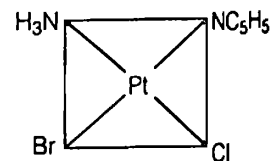
#### Geometric isomerism of metals of C.N. 4

For square planar complex  $Ma_4$ ,  $Ma_3b$  or  $Mab_3$  where  $a$  and  $b$  etc., are monodentate ligands, geometrical isomerism is not possible. However, square planar complexes of the type  $Ma_2b_2$ ,  $Ma_2bc$ ,  $Mabcd$  and  $M(AA)_2$ ,  $M(AB)_2$ —when  $AA$  and  $AB$  represent symmetrical and unsymmetrical chelating agents to give geometrical isomers.

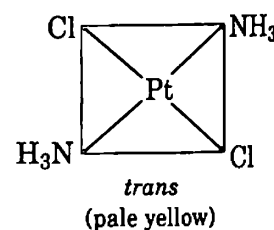
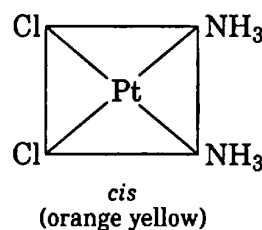
| Type      | Compound         | Isomers                                                                                           |
|-----------|------------------|---------------------------------------------------------------------------------------------------|
| $Ma_2b_2$ | $Pt(NH_3)_2Cl_2$ | <i>cis</i> and <i>trans</i> as in (i)                                                             |
| $Ma_2bc$  | $Pt(NH_3)_2ClBr$ | <br><i>cis</i> |



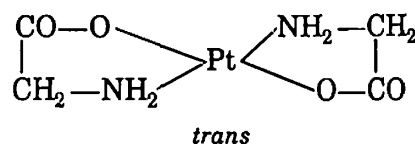
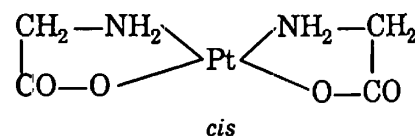
$Mabcd$   $Pt(NH_3)(C_5H_5N)(Cl)(Br)$



(i)  $[Pt(NH_3)_2Cl_2]$  can exist as two geometric isomers:

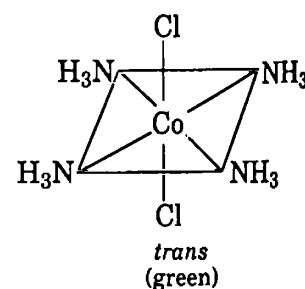
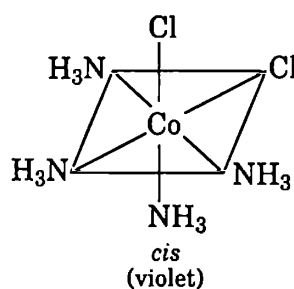


(ii)  $[Pt(Gly)_2]$

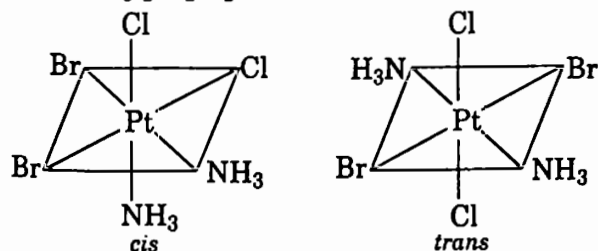


#### Geometric isomerism of metals of C.N. 6

(i)  $[Co(NH_3)_4Cl_2]^+$  can exist as

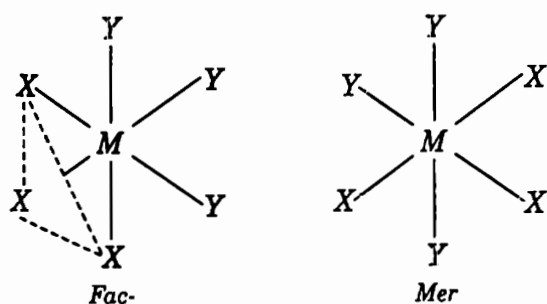


(ii)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2\text{Br}_2]$  can exist as

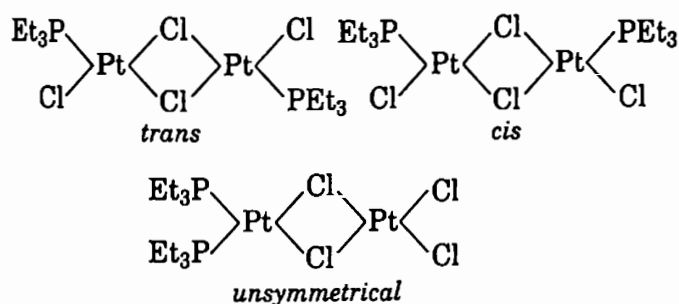


There are so many other arrangements also.

Another type of geometrical isomerism occurs in octahedral coordination entities of the type  $[\text{MX}_3\text{Y}_3]$  like  $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$ . If each trio of donor atoms occupy adjacent positions at the corners of an octahedral face, it is called **facial (fac-) isomer**. When the positions are around the meridian of the octahedron the isomer is called **meridional (mer-) isomer**.



Bridged binuclear complexes like  $[\text{Pt}(\text{PEt}_3)\text{Cl}_2]_2$  may exist in three isomers forms

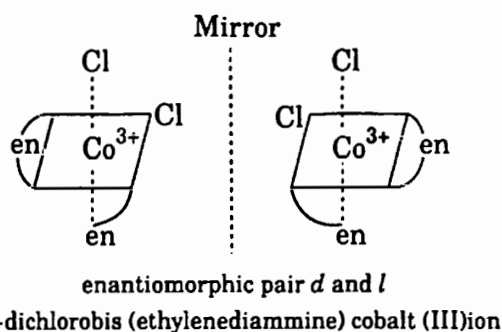
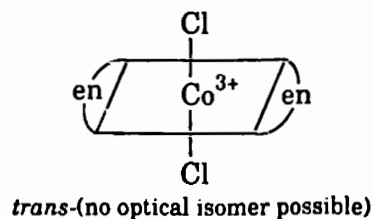


As we increase the number of different ligands, the possible number of isomers increases.

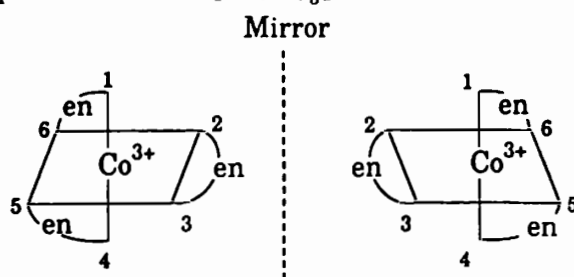
## (b) Optical Isomerism

If a molecule is asymmetric, it can't be superimposed on its mirror image. The two forms have the type of symmetry shown by the left and right hands and are called **enantiomorphous pair**. The two forms are called **optical isomer**. They are called either *dextro* or *laevo* (*d* or *l*). This depends on the direction they rotate the plane of polarised light in a polarimeter.

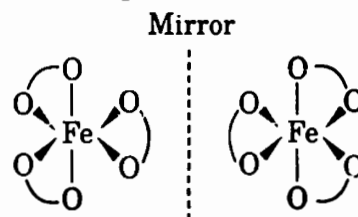
- Optical isomerism is common in octahedral complexes involving bidentate groups.
- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  exists as *cis*- and *trans*-isomers. But *cis*-isomer can have *d* and *l*-optical isomers.



- Optical isomers of  $[\text{Co}(\text{en})_3]^{3+}$  are:



- In  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ ,  $\text{C}_2\text{O}_4^{2-}$  is a bidentate ligand and that three  $\text{C}_2\text{O}_4^{2-}$  ligands mean that the metal has a coordination number of 6. Mirror images of complex  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  are not superimposable; therefore two optical isomers are possible.



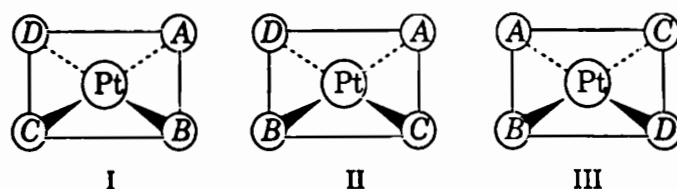
Non-superimposable mirror images of  $[\text{Fe}(\text{ox})_3]^{3-}$

**Illustration 2** If A, B, C, and D are four different ligands,

- how many geometric isomers will be found for square planar  $[\text{PtABCD}]^{2+}$ ?
- will tetrahedral  $[\text{ZnABCD}]^{2+}$  display optical isomerism?

**Solution** (a) Following three different isomers are possible for the square planar  $[\text{PtABCD}]^{2+}$ .

(You may write others but they will be identical)





(b) There is chirality and enantiomers do not superimpose hence,  $[\text{ZnABCD}]^{2+}$  displays optical isomerism.

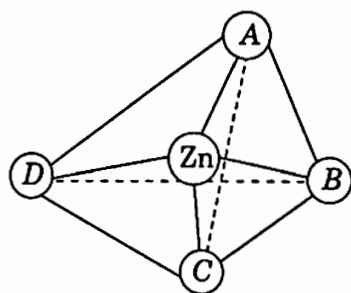
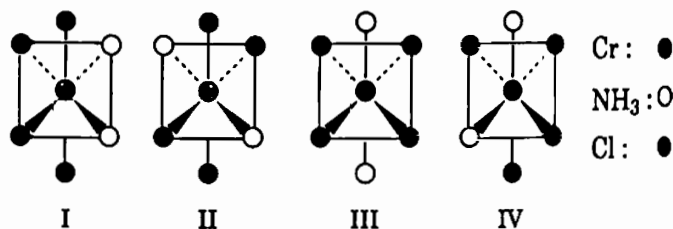


**Illustration 3** Consider the given isomers of  $[\text{Cr}(\text{NH}_3)_2\text{Cl}_4]^-$

(a) Label the isomers as *cis* or *trans*.

(b) Which isomers are identical and which are different.

(c) Do any of these isomers exist as enantiomers.



**Solution** (a) I, IV *cis*; II, III *trans*

(b) I and IV are the same; II and III are the same

(c) None of the isomers exists as enantiomers because their mirror images are identical.

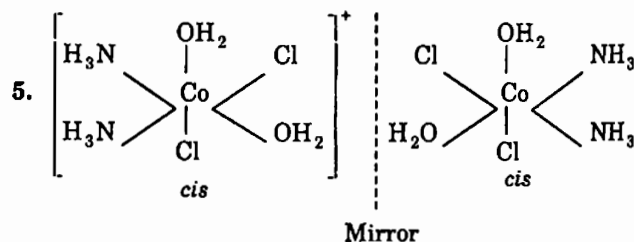
## Target Practice 1

- Determine the oxidation state of the coordinated metal atom in each of the following compounds :
  - $\text{K}[\text{Co}(\text{NH}_3)_2(\text{CN})_4]$  .....
  - $\text{Os}(\text{CO})_5$  .....
  - $\text{Na}[\text{Co}(\text{H}_2\text{O})_3(\text{OH})_3]$  .....
- Write formulas of
  - Sodium tricarbonatocobaltate (III) .....
  - Diamminediaquadichloroplatinum (IV) bromide .....
  - Sodium tetranitratoborate (III) .....
- How might one distinguish between the following isomers?
  - $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  .....  

I
II
  - cis* and *trans*- $[\text{CoCl}_2(\text{en})_2]\text{Cl}$  .....
- Give examples of the following types of isomerisation.
  - Hydrate isomerism .....
  - Ionisation isomerism .....
  - Geometrical isomerism .....
- Suppose the complex ion  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2]^+$  is synthesised with two ammine ligands *cis* to each other, the two aqua ligands *cis* to each other, and two chloro ligands *cis* to each other. Is this complex optically active.
- Give the formulae of the following coordination complexes :
  - A  $\text{Ni}^{2+}$  ion is bound to two water molecules and two bidentate oxalate ions. ....
  - A  $\text{Co}^{3+}$  ion is bound to one  $\text{Cl}^-$  ion, one ammonia molecule, and two bidentate ethylenediamine (en) molecules .....
- Identify the type of isomerism shown by
  - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  .....
  - $[\text{Pt}(\text{NH}_3)_2(\text{CN})_2]$  (square planar) .....
  - $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  (tetrahedral) .....
  - $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  .....
  - $[\text{Co}(\text{NH}_3)_5(\text{SCN})]^{2+}$  .....

## Answers

- (a) +3 (b) zero (c) +2
- (a)  $\text{Na}_3[\text{Co}(\text{CO}_3)_3]$   
(b)  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2]\text{Br}_2$   
(c)  $\text{Na}[\text{B}(\text{NO}_3)_4]$
- (a) I gives white precipitate with  $\text{BaCl}_2(\text{aq})$  while II gives yellow precipitate with  $\text{AgNO}_3(\text{aq})$ .  
(b) Dipole moment of *cis*- > *trans*-
- (a)  $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$  and  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$   
(b)  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$   
(c)  $\text{MCl}_2\text{Br}_2$  (square planar) will form *cis*- and *trans*- isomers



Mirror images are not superimposable hence the complex is optically active (being chiral)

- (a)  $[\text{Ni}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]^{2-}$  (b)  $[\text{Co}(\text{NH}_3)(\text{en})_2\text{Cl}]^{2+}$
- (a) geometrical *cis*, *trans*- (b) geometrical *cis*-, *trans*-  
(c) only single structure is possible (d) optical and  
(e) linkage S-bonded  $\text{SCN}^-$  N-bonded  $\text{NCS}^-$

## Practice Exercise 1

- Classify double salts and coordination compounds out of
  - $3\text{NaF} \cdot \text{AlF}_3$  which does not give tests of  $\text{F}^-$  and  $\text{Al}^{3+}$  ions
  - $4\text{KCN} \cdot \text{Fe}(\text{CN})_2$  which does not give tests of  $\text{CN}^-$  and  $\text{Fe}^{2+}$
  - Alum which gives tests of  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  ions
  - Mohr's salt which gives tests of  $\text{NH}_4^+$ ,  $\text{Fe}^{2+}$  and  $\text{SO}_4^{2-}$  ions.

- What is the type of complex formed, cationic or anionic, in the following?

Also designate the coordinate ion in each case.

- $\text{FeSO}_4 + \text{KCN} \longrightarrow$
- $\text{CoCl}_2 + \text{KNO}_2 \longrightarrow$
- $\text{PtCl}_4 + \text{KCl} \longrightarrow$
- $\text{AgCl} + \text{NH}_3 \longrightarrow$
- $\text{AgBr} + \text{Na}_2\text{S}_2\text{O}_3 \longrightarrow$
- $\text{HgI}_2 + \text{KI} \longrightarrow$

- Following complexes ionise in aqueous solution. What are the ions in each case?

- $\text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$
- $\text{NaAlO}_2$
- $\text{Ni}(\text{CO})_4$
- $\text{Na}_3\text{AlF}_6$
- $(\text{NH}_4)_2\text{PtCl}_6$
- $\text{Na}_2[\text{Ni}(\text{CN})_4]$

- When aqueous KCN is added to a solution of  $\text{CuSO}_4$ , a white precipitate, soluble in excess of KCN, is formed. No precipitate is formed when  $\text{H}_2\text{S}$  gas is bubbled through the solution at this point. Explain.

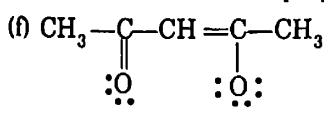
- (a) Formation of  $[\text{Ni}(\text{en})_3]^{2+}$  from  $\text{Ni}^{2+}$  and ethylenediamine is a Lewis acid-base reaction. Explain.

- Identify the Lewis acid and Lewis base in the reaction of oxalate ions ( $\text{C}_2\text{O}_4^{2-}$ ) with  $\text{Fe}^{3+}$  to give  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ .

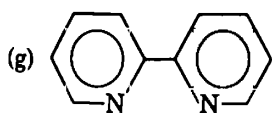
- Classify the following ligands as unidentate, bidentate, .... polydentate:

- $\text{CH}_3\text{COO}^-$
- $:\text{OCN}^-$
- $:\text{NCO}^-$
- $\text{CO}_3^{2-}$
- $\text{NH}_2-\text{CH}_2\text{CH}(\text{CH}_3)-\text{NH}_2$

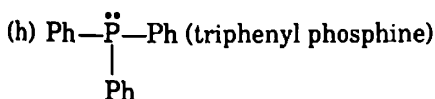
(propylene diamine written as **pn**),



(acetylacetonato written as **acac**)



(2,2'-bipyridine written as **bipy**)

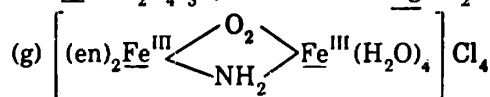


- Write the formula of

- a complex ion having  $\text{Co}^{2+}$  as the central ion and two  $\text{NH}_3$  molecules and four  $\text{Cl}^-$  ions as ligands,
- a complex ion of manganese (III) having coordination number of 6 and  $\text{CN}^-$  as ligands,
- a coordination compound comprised of two types of complex ions; one is a complex of  $\text{Cr}(\text{III})$  with ethylenediamine (**en**), having a coordination number of 6 and the other is a complex of  $\text{Ni}(\text{II})$  with  $\text{CN}^-$  and having a coordination number of 5.

- What are the coordination numbers of the underlined atoms in the following? Also specify the charge on the complex, oxidation number of the metal ion has been given :

- $[\text{Fe}^{\text{II}}(\text{CN})_6]$
- $[\text{Ni}^{\text{I}}(\text{CO})_4]$
- $[\text{Ca}^{\text{II}}(\text{EDTA})]$
- $[\text{Pt}^{\text{IV}}(\text{en})\text{Cl}_2\text{Br}_2]$



- One mole of  $\text{CoCl}_3 \cdot 4\text{NH}_3$  on reaction with excess of  $\text{AgNO}_3$  gives one mole of white precipitate. What is the complex? What is the coordination number of cobalt?

- Give the oxidation number of the metals in the following species:

- $\text{K}_3[\text{Fe}(\text{CN})_6]$
- $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$
- $[\text{Ni}(\text{CN})_4]^{2-}$
- $\text{Na}_2\text{MoO}_4$
- $\text{Fe}(\text{CO})_5$
- $\text{MgWO}_4$

- Complete the following statements for the complex ion:  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$

- The oxidation number of Cr is .....
- The coordination number of Cr is .....
- ..... is a bidentate ligand

- Name the following compounds:

- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{NO}_3$
- $[\text{Pt}(\text{en})\text{Cl}_4]$
- $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$
- $\text{K}_3[\text{Co}(\text{ONO})_6]$
- $\text{Na}_2[\text{Zn}(\text{EDTA})]$
- $[\text{Ru}(\text{en})_2\text{Br}_2]\text{Br}$
- $[\text{Pt}(\text{Py})_4][\text{PtF}_4]$

- Write the formulae of each of the following compounds :

- cesium trichlorofluoro iodate (III)
- tris (ethylenediamine)nickel (II) nitrate
- potassium dibromodioxalatocobaltate (III)
- pentamminechlorochromium (III) sulphate
- ethylenediaminetetraiodoplatinum (IV)
- potassium tetrafluoroargentate (III)
- rubidium ethylenediaminetetraacetatocobaltate (III) dihydrate

- Calculate EAN of the metal in the following complexes, and compare it with the atomic number of the nearest rare gas:

- $\text{AuCl}_2$
- $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$
- $\text{CdI}_4^{2-}$
- $[\text{Cr}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{2+}$
- $\text{Co}(\text{NO}_2)_6^{3-}$
- $\text{Fe}(\text{CO})_5$
- $[\text{Ca}(\text{EDTA})]^{2-}$
- $[\text{Ni}(\text{Py})(\text{en})(\text{NH}_3)_3]^{2+}$
- $[\text{Zn}(\text{OH})_4]^{2-}$
- $\text{HgI}_4^{2-}$

- Determine EAN of iron in

- $\text{Fe}(\text{CO})_5$
- $\text{Fe}(\text{C}_5\text{H}_5)_2$

- Predict value of  $x$  in

- $\text{H}_x\text{Cr}(\text{CO})_5$
- $\text{H}_x\text{Co}(\text{CO})_4$

- Make hydrate isomers of:

- $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_3$
- $[\text{Cu}(\text{H}_2\text{O})_4]\text{Cl}_2$

Also arrange them in the increasing conducting power.

- One cationic complex has two isomers A and B. Each has one  $\text{Co}^{3+}$ , five  $\text{NH}_3$ , one  $\text{Br}^-$  and one  $\text{SO}_4^{2-}$  stoichiometrically. A gives white ppt. with  $\text{BaCl}_2$  while B give yellow ppt. with  $\text{AgNO}_3$ . What are A and B? What is the type of isomerism shown?

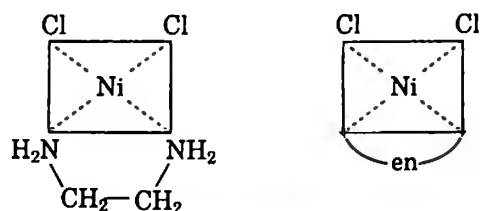
- Two isomers of  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$  differ in colour. What is the cause? If each reacts with excess  $\text{AgNO}_3$ , what is precipitated and how much per mole of the complex?

- Which of the following can show coordination isomerism?

- $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$
- $[\text{Fe}(\text{NH}_3)_6]_2[\text{Pt}(\text{CN})_6]_3$
- $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{C}_2\text{O}_4)_3]$
- $[\text{Pt}(\text{en})_3](\text{SO}_4)_2$

24. A complex has a composition corresponding to the formula  $\text{CoBr}_2\text{Cl} \cdot 4\text{NH}_3$ . What is the structural formula of the complex? Conductance measurements show two ions per formula unit. Silver nitrate solution gives ppt. of  $\text{AgCl}$  but no  $\text{AgBr}$ . Write the structural formula of an isomer.
25. How many geometric isomers are in the following species?  
(a)  $[\text{Co}(\text{NH}_3)_2\text{Cl}_4]^-$  (b)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
26. Draw structures of all the geometric and optical isomers of each of the following cobalt complexes:  
(a)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  (b)  $[\text{Co}(\text{en})_3]^{3+}$
27. Which of the following complexes are chiral?  
(a)  $[\text{Pt}(\text{en})\text{Cl}_2]$  (b)  $\text{cis-}[\text{Co}(\text{NH}_3)_4\text{Br}_2]^+$   
(c)  $\text{cis-}[\text{Cr}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$  (d)  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

## Answers



23. (b) and (e) for structure see text.  
 24.  $[\text{Co}(\text{NH}_3)_4\text{BrCl}]\text{Cl}$ , isomer  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$   
 25. (a) 2 (b) 2  
 26. (a) Two geometrical isomers  
 (b) Two optical isomer. For structures see text  
 27. (c) and (d)

## Werner Theory of Coordination Compounds

- Beginning of the coordination chemistry is not based on the first formation of  $\text{CoCl}_3 \cdot 6\text{NH}_3$  by Tassqert but is actually considered based on the outstanding work of the Alsatian-Swiss chemist Alfred Werner in 1892.
- Werner prepared and isolated many different coordination compounds from  $\text{CoCl}_3$  and  $\text{NH}_3$  like
  - (a)  $\text{CoCl}_3 \cdot 6\text{NH}_3$   $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  orange-yellow
  - (b)  $\text{CoCl}_3 \cdot 5\text{NH}_3$   $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  violet (purple)
  - (c)  $\text{CoCl}_3 \cdot 4\text{NH}_3$   $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  violet
  - (d)  $\text{CoCl}_3 \cdot 3\text{NH}_3$   $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  green

Treatment of these compounds with aqueous hydrochloric acid did not remove the ammonia, which suggested that the ammonia was somehow closely bound with the cobalt ions. Treatment with aqueous silver nitrate at 273 K, however gave interesting results. One mole each of the complexes (a), (b) and (c) gave respectively thus, two and one mole of white precipitates of  $\text{AgCl}$ , with excess of  $\text{AgNO}_3$ . Complex (d) did not give the precipitate at all.

## Postulates

- There are two types of valencies shown by central metal/metal ion in a compound :
  - (a) primary
  - (b) secondary
- Primary valency corresponds to oxidation number and secondary valency corresponds to coordination number.

- In the complex  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , primary valency of Co is **three** and secondary valency **six**.
- Primary valency is satisfied by negative ions (anions) while secondary valency is satisfied by ligands which can be neutral, and as well as negative (positive in rare cases)
  - In  $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$ , six  $\text{NH}_3$  ligands satisfy secondary valencies while three  $\text{Cl}^-$  satisfy primary valencies.
  - In  $[\text{Co}^{\text{II}}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{SO}_4$ , four  $\text{NH}_3$  and two  $\text{H}_2\text{O}$  (ligands) satisfy secondary and one  $\text{SO}_4^{2-}$  satisfy primary valencies.
- Ligands/ions attached by secondary valency do not ionise while ions attached by primary valency ionise.
 
$$\text{K}_4[\text{Fe}(\text{CN})_6] \rightleftharpoons 4\text{K}^+ + [\text{Fe}(\text{CN})_6]^{4-}$$

$$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4 \rightleftharpoons [\text{Pt}(\text{NH}_3)_6]^{4+} + 4\text{Cl}^-$$
- The secondary valencies are directional and are responsible for the isomerism in complexes.
- Primary valency in the complex is represented by ..... while secondary valency by ———.
- In all cases, metal or metal ion should satisfy primary and secondary valencies both. Some negative ions may satisfy primary as well as secondary valencies (**dual nature**). In the complexes, they are represented as .....

## Werner's Representation

Consider the case of  $\text{CoCl}_3 \cdot x\text{NH}_3$   
 where maximum value of  $x = \text{C.N. of Co(III)} = 6$   
 and minimum value of  $x = \text{C.N.} - \text{O.N.} = 3$   
 Various structures are summarised in Table 18.6.

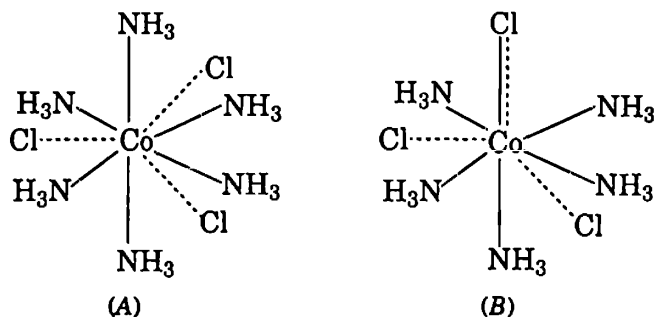
Table 18.6 Werner's Coordination Compounds

| Werner complex                         | Modern notation                                  | Ionisation                                                  | Secondary valency satisfied by                      | Primary valency satisfied by                                             |
|----------------------------------------|--------------------------------------------------|-------------------------------------------------------------|-----------------------------------------------------|--------------------------------------------------------------------------|
| (A) $\text{CoCl}_3 \cdot 6\text{NH}_3$ | $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$          | $[\text{Co}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-$            | six ( $\text{NH}_3$ )                               | three ( $\text{Cl}^-$ )                                                  |
| (B) $\text{CoCl}_3 \cdot 5\text{NH}_3$ | $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ | $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + 2\text{Cl}^-$   | five ( $\text{NH}_3$ ) and one ( $\text{Cl}^-$ )    | three ( $\text{Cl}^-$ ) including one ( $\text{Cl}^-$ ) with dual nature |
| (C) $\text{CoCl}_3 \cdot 4\text{NH}_3$ | $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ | $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{Cl}^-$     | four ( $\text{NH}_3$ ) and two ( $\text{Cl}^-$ )    | three ( $\text{Cl}^-$ ) including two ( $\text{Cl}^-$ ) with dual nature |
| (D) $\text{CoCl}_3 \cdot 3\text{NH}_3$ | $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$          | $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$<br>(single species) | three ( $\text{NH}_3$ ) and three ( $\text{Cl}^-$ ) | three ( $\text{Cl}^-$ ) all with dual nature                             |

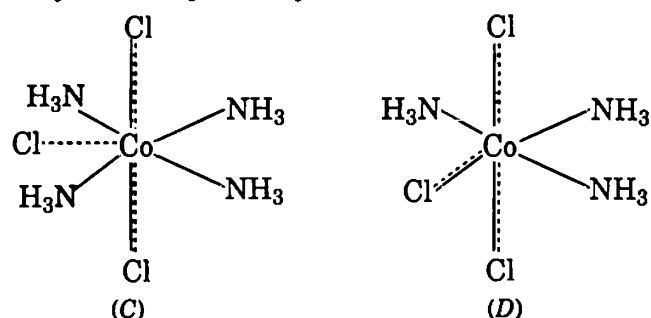
- From the Table 18.6, it is clear that conduction of the complexes which depends on the number of ions will be in order:

$$D < C < B < A$$

- They are represented as :



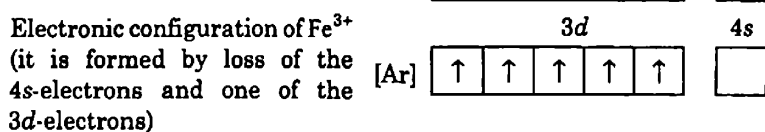
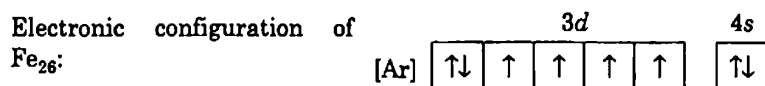
[only  $\text{Cl}^-$  ions joined by (.....) will ionise].



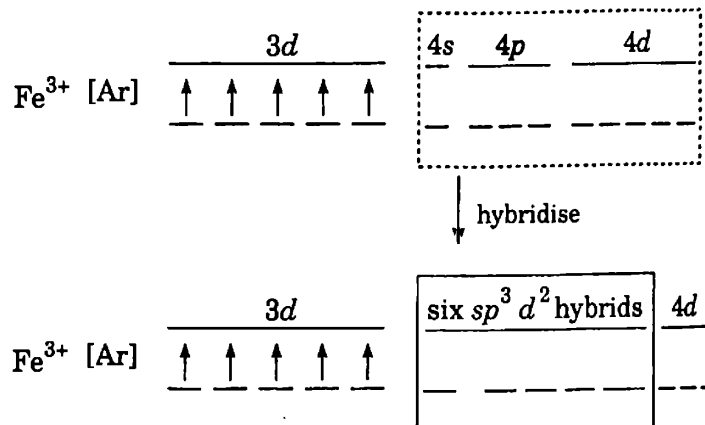
## Bonding in Complexes

**Valence Bond Theory (VBT)** One way to think about bonds between a metal ion and its ligands is based on coordinate covalency. The central ion furnishes the orbitals and the ligands furnish electron pairs (refer Chapter-7). Although this view is now considered inadequate, it does account for the observed coordination number of the central ion, and it also describes the geometric structure of the complex ion.

Let us study some complexes to see how the valence bond theory explains their properties. Take example of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ . The complex is known to be paramagnetic, with a magnetic moment corresponding to five unpaired electrons. This can be described if we follow:

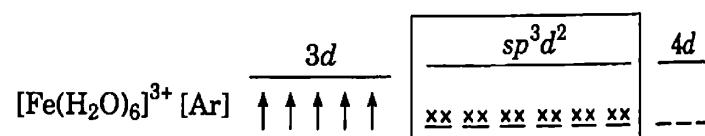


To account for the experimentally observed fact that  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  has five unpaired electrons, each 3d-orbitals is assumed to have one unpaired electrons in the complex. The vacant  $4d_{x^2-y^2}$  and  $4d_{z^2}$  orbitals are hybridised with the vacant 4s- and 4p-orbitals.



Each of the six  $\text{H}_2\text{O}$  ligands donates one electron pair into one of the six  $sp^3d^2$ -orbitals, forming six coordinate-covalent bonds. These donated electrons (from O of  $\text{H}_2\text{O}$  ligands) have been represented as "x" rather than " $\uparrow$ ". These are the only bonding electrons; none of the 3d-electron of iron is involved in bonding.

A set of outer d orbitals is used in hybridisation, and hence  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is called an **outer orbital complex**.

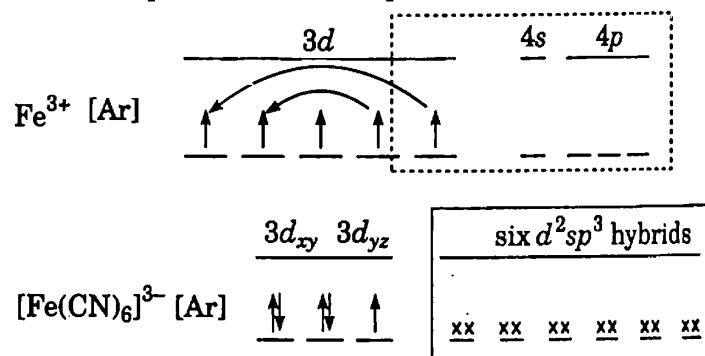


In deciding whether the hybridisation at the central metal ion of octahedral complexes is  $sp^3d^2$  (outer orbital) or  $d^2sp^3$  (inner orbital) we must know the results of magnetic measurements. These indicate the number of unpaired electrons ( $N$ ). Magnetic moment is given by

$$\mu = \sqrt{N(N+2)} \text{ BM}$$

(BM is Bohr Magneton)

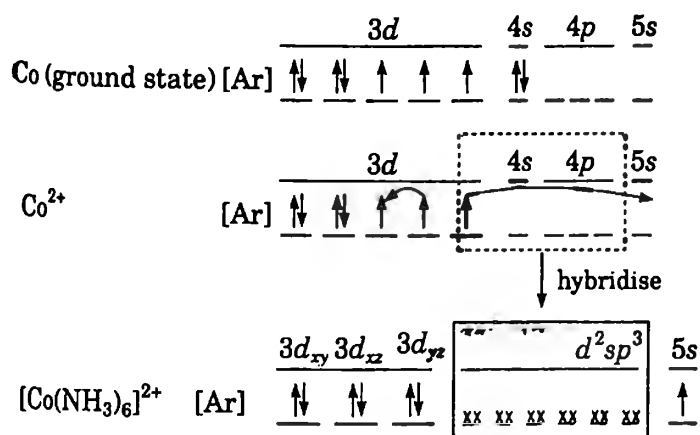
In  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $\text{Fe}^{3+}$  is involved (a  $d^5$  ion). But magnetic measurements indicate only one unpaired electron per iron atom. The  $3d_{x^2-y^2}$  and  $3d_{z^2}$  orbitals (rather than those in 4d-shell) are involved in  $d^2sp^3$  hybridisation. All but one of the non-bonding 3d-electrons of  $\text{Fe}^{3+}$  are paired in this complex.



Only inner d-orbitals are used in hybridisation, hence  $[\text{Fe}(\text{CN})_6]^{3-}$  is called an **inner orbital complex**. Additional illustrations have been summarized in Table 18.7 (refer Chapter-7)

**Illustration 1** Explain the paramagnetic behaviour of  $[\text{Co}(\text{NH}_3)_6]^{2+}$ .

**Solution** Oxidation state of Co = + 2



When hybridisation occurs, one of the 3d-electrons is excited to 5s-orbital.

The suggested bonding for  $[\text{Co}(\text{NH}_3)_6]^{2+}$  is consistent with the fact that this complex is easily oxidised to  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , an extremely stable complex ion.

Since there exists one unpaired electron, this complex ion is paramagnetic. Magnetic moment is given by:

$$\mu = \sqrt{N(N+2)} \text{ B.M.} = \sqrt{3} \text{ BM}$$

Table 18.7 Bonding and Hybridisation in Some Octahedral Complexes

| Metal ion                     | Outer electron configuration                                                                   | Complex ion                       | Type                            | Outer electron configuration                                                       |
|-------------------------------|------------------------------------------------------------------------------------------------|-----------------------------------|---------------------------------|------------------------------------------------------------------------------------|
| $\text{Cr}^{3+}$<br>( $d^3$ ) | $3d$ $\uparrow$ $\uparrow$ $\uparrow$ $4s$ $4p$ $4d$                                           | $[\text{Cr}(\text{NH}_3)_6]^{3+}$ | inner orbital<br>(paramagnetic) | $3d$ $\uparrow$ $\uparrow$ $\uparrow$ $d^2sp^3$ $4d$                               |
| $\text{Mn}^{2+}$<br>( $d^5$ ) | $3d$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $4s$ $4p$ $4d$                     | $[\text{Mn}(\text{CN})_6]^{2-}$   | inner orbital<br>(paramagnetic) | $3d$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ $d^2sp^3$ $4d$           |
| $\text{Fe}^{2+}$<br>( $d^6$ ) | $3d$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $4s$ $4p$ $4d$           | $[\text{Fe}(\text{CN})_6]^{4-}$   | inner orbital<br>(diamagnetic)  | $3d$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $d^2sp^3$ $4d$ |
| $\text{Co}^{3+}$<br>( $d^6$ ) | $3d$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $4s$ $4p$ $4d$           | $[\text{Co}(\text{NH}_3)_6]^{3+}$ | inner orbital<br>(diamagnetic)  | $3d$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $d^2sp^3$ $4d$ |
|                               |                                                                                                | $[\text{CoF}_6]^{3-}$             | outer orbital<br>(paramagnetic) | $3d$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$ $\uparrow$ $sp^3d^2$ $4d$          |
| $\text{Co}^{2+}$<br>( $d^7$ ) | $3d$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $4s$ $4p$ $4d$           | $[\text{Co}(\text{OH}_2)_6]^{2+}$ | outer orbital<br>(diamagnetic)  | $3d$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ $sp^3d^2$ $4d$           |
| $\text{Ni}^{2+}$<br>( $d^8$ ) | $3d$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$ $\uparrow$ $4s$ $4p$ $4d$ | $[\text{Ni}(\text{OH}_2)_6]^{2+}$ | outer orbital<br>(paramagnetic) | $3d$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ $sp^3d^2$ $4d$           |

## Crystal Field Theory

The valence-bond theory has some shortcomings:

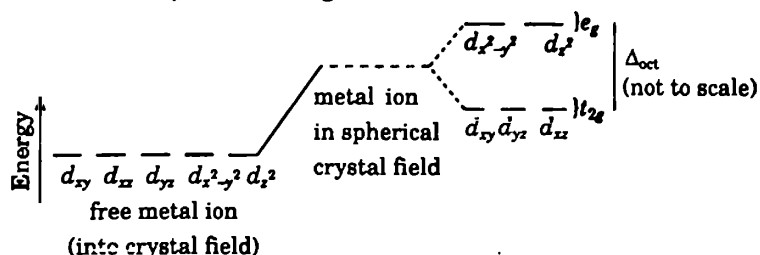
- It does not provide insight into the origin of the characteristic colour of the complex ions.
- It does not distinguish between weak and strong ligands.
- It does not give quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- There is no quantitative interpretation of magnetic data.
- It does not explain why some complexes are inner-orbital complex and some complexes are outer-orbital.

Most of the shortcomings of VBT of coordination compounds were removed in **Crystal Field Theory (CFT)**. It attributes partial covalent character and partial ionic character to bonds.

### Complexes with C.N. 6 (Octahedral Crystal Field)

- Five  $d$ -orbitals ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ,  $d_{x^2-y^2}$  and  $d_{z^2}$ ) are of equal energy and thus are degenerate.
- The  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals are directed along a set of mutually perpendicular  $x$ ,  $y$  and  $z$ -axes. As a group, these orbitals are called  **$e_g$  orbitals**.
- The  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals, lie between the axes and collectively called  **$t_{2g}$  orbitals**.
- The ligand donor atoms approach the metal ion along the axes to form octahedral complexes. Crystal field theory proposes that the approach of the six donor atoms along the axes sets up an electric field (crystal field). Electrons on the ligand repel electrons in  $e_g$  orbitals on the metal ion more strongly than they repel those in  $t_{2g}$  orbitals. This removes the degeneracy of the set of  $d$ -orbitals and splits them into two sets, the  $e_g$  set at higher energy and the  $t_{2g}$  set at lower energy.

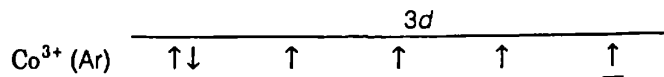
The energy separation between the two sets is called  $\Delta_{\text{octahedral}}$  or  $\Delta_{\text{oct}}$ . It is proportional to the crystal field of the strength of the ligands.



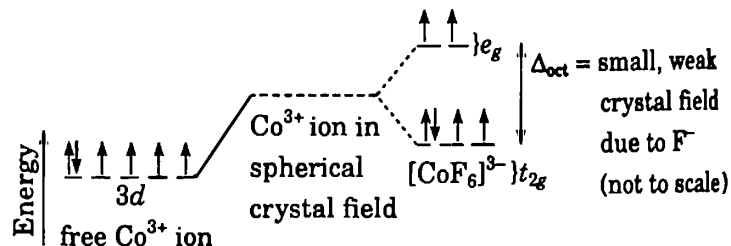
- The  $d$ -electrons on a metal ion occupy the  $t_{2g}$  set in preference to the higher energy,  $e_g$  set. Electrons that occupy the  $e_g$  orbitals are strongly repelled by the

relatively close approach of ligands. Electron in  $e_g$  set tends to destabilise octahedral complexes.

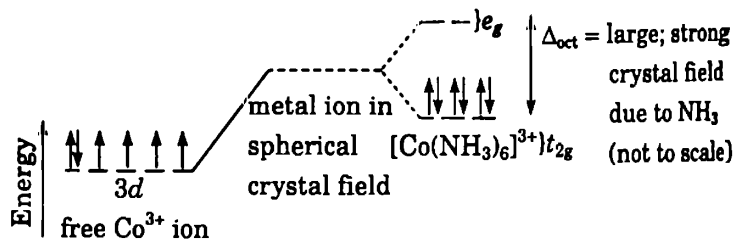
- Based on valence bond theory,  $[\text{CoF}_6]^{3-}$  is a paramagnetic outer orbital complex while  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is a diamagnetic inner orbital complex. Both contain  $d^6 \text{Co}^{3+}$  ions (four unpaired electron) in its  $3d$ -orbitals.



Magnetic measurements indicate that  $[\text{CoF}_6]^{3-}$  also has four unpaired electrons per ion. Thus, there must be four electrons in  $t_{2g}$  orbitals and two in  $e_g$  orbitals.



On the other hand,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is diamagnetic, thus, all the six  $d$ -electrons must be paired in the  $t_{2g}$  orbitals.



The difference in configuration between  $[\text{CoF}_6]^{3-}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is due to the relative magnitude of the crystal field splitting,  $\Delta_{\text{oct}}$ , caused by the different crystal field strengths of  $\text{F}^-$  and  $\text{NH}_3$ . The  $\text{NH}_3$  molecule interacts with vacant metal orbitals more strongly than the  $\text{F}^-$  ion does.

$$\Delta_{\text{oct}} \text{ for } [\text{Co}(\text{NH}_3)_6]^{3+} > \Delta_{\text{oct}} \text{ for } [\text{CoF}_6]^{3-}$$

The crystal field splitting for  $[\text{CoF}_6]^{3-}$  complex ion is very small and thus, an energetically more favourable condition may arise if two electrons remain unpaired in the anti-bonding,  $e_g$  orbitals. After all  $d$ -orbitals are half-filled, additional electrons will pair with electrons in  $t_{2g}$  set. This is the case for  $[\text{CoF}_6]^{3-}$ , which is called a **high spin complex**.

For  $[\text{CoF}_6]^{3-}$ :  $\text{F}^-$  is a weak field ligand, so  $\Delta_{\text{oct}} < P$  (electron pairing energy), thus, **high spin complex**.

A high spin complex in crystal field terminology corresponds to an outer orbital complex in VBT.

For  $[\text{Co}(\text{NH}_3)_6]^{3+}$ :  $\text{NH}_3$  is a strong field ligand so that  $\Delta_{\text{oct}} > P$ , thus **low spin complex**.

A low spin complex corresponds to an inner orbital complex.

- Low spin configurations exist only for octahedral complexes having metal ions with  $d^4$ ,  $d^6$ ,  $d^8$  and  $d^9$  configurations. For  $d^1 - d^3$  and  $d^8 - d^{10}$  ions configuration is designated as high spin. All  $d^n$  possibilities have been shown in Table 18.8

Table 18.8 Electron Configurations and Crystal Field Stabilisation Energies for High and Low Spin Octahedral Complexes

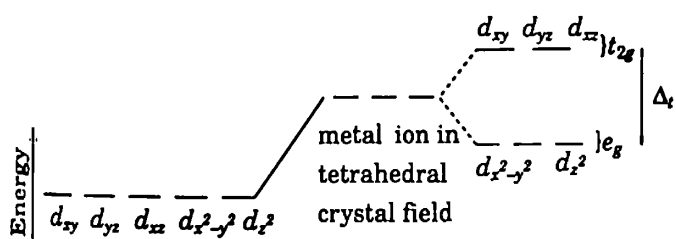
| Configuration | $d^1$                                              | $d^2$                                              | $d^3$                                              | $d^4$                                                                  | $d^5$                                                                  | $d^6$                                                                               | $d^7$                                                                               | $d^8$                                                                                        | $d^9$                                                                                                   | $d^{10}$                                                                                                           |
|---------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|------------------------------------------------------------------------|------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|
| Examples      | $Ti^{3+}$                                          | $Ti^{2+}, V^{3+}$                                  | $V^{2+}, Cr^{3+}$                                  | $Mn^{3+}, Re^{3+}$                                                     | $Mn^{2+}, Fe^{3+}$                                                     | $Fe^{2+}, Pd^{4+}$                                                                  | $Co^{2+}, Rh^{2+}$                                                                  | $Ni^{2+}, Pt^{2+}$                                                                           | $Cu^{2+}$                                                                                               | $Zn^{2+}, Ag^+$                                                                                                    |
| High spin     | $e_g$ — —<br>$t_{2g}$ $\uparrow$ — —               | $e_g$ — —<br>$t_{2g}$ $\uparrow \uparrow$ —        | $e_g$ — —<br>$t_{2g}$ $\uparrow \uparrow \uparrow$ | $e_g$ $\uparrow$ — —<br>$t_{2g}$ $\uparrow \uparrow \uparrow$          | $e_g$ $\uparrow \uparrow$ — —<br>$t_{2g}$ $\uparrow \uparrow \uparrow$ | $e_g$ $\uparrow \uparrow$ — —<br>$t_{2g}$ $\uparrow \downarrow \uparrow \uparrow$   | $e_g$ $\uparrow \uparrow$ — —<br>$t_{2g}$ $\uparrow \downarrow \uparrow \downarrow$ | $e_g$ $\uparrow \uparrow$ — —<br>$t_{2g}$ $\uparrow \downarrow \uparrow \downarrow \uparrow$ | $e_g$ $\uparrow \downarrow \uparrow$ — —<br>$t_{2g}$ $\uparrow \downarrow \uparrow \downarrow \uparrow$ | $e_g$ $\uparrow \downarrow \uparrow \downarrow$ — —<br>$t_{2g}$ $\uparrow \downarrow \uparrow \downarrow \uparrow$ |
| CFSE          | $-\frac{2}{5} \Delta_o$                            | $-\frac{4}{5} \Delta_o$                            | $-\frac{6}{5} \Delta_o$                            | $-\frac{3}{5} \Delta_o$                                                | 0                                                                      | $-\frac{2}{5} \Delta_o$                                                             | $-\frac{4}{5} \Delta_o$                                                             | $-\frac{5}{5} \Delta_o$                                                                      | $-\frac{3}{5} \Delta_o$                                                                                 | 0                                                                                                                  |
| Low spin      | $e_g$ — —<br>$t_{2g}$ $\uparrow \uparrow \uparrow$ | $e_g$ — —<br>$t_{2g}$ $\uparrow \uparrow \uparrow$ | $e_g$ — —<br>$t_{2g}$ $\uparrow \uparrow \uparrow$ | $e_g$ $\uparrow \uparrow$ — —<br>$t_{2g}$ $\uparrow \uparrow \uparrow$ | $e_g$ $\uparrow \uparrow$ — —<br>$t_{2g}$ $\uparrow \uparrow \uparrow$ | $e_g$ $\uparrow \uparrow$ — —<br>$t_{2g}$ $\uparrow \downarrow \uparrow \downarrow$ | $e_g$ $\uparrow$ — —<br>$t_{2g}$ $\uparrow \downarrow \uparrow \downarrow$          | $e_g$ — —<br>$t_{2g}$ $\uparrow \downarrow \uparrow \downarrow$                              | $e_g$ — —<br>$t_{2g}$ $\uparrow \downarrow \uparrow \downarrow$                                         | $e_g$ — —<br>$t_{2g}$ $\uparrow \downarrow \uparrow \downarrow$                                                    |
| CFSE          | Same as high spin                                  | Same as high spin                                  | Same as high spin                                  | $-\frac{8}{5} \Delta_o$                                                | $-\frac{10}{5} \Delta_o$                                               | $-\frac{12}{5} \Delta_o$                                                            | $-\frac{9}{5} \Delta_o$                                                             | Same as high spin                                                                            | Same as high spin                                                                                       | Same as high spin                                                                                                  |

### Complexes with C.N. 4 (Tetrahedral Crystal Field)

In tetrahedral complex formation, the  $d$ -orbital splitting is inverted and smaller as compared to the octahedral field splitting. If  $\Delta_t$  is the magnitude of energy separation in tetrahedral crystal field, then for the same metal, the same ligands and metal-ligand bond distance,

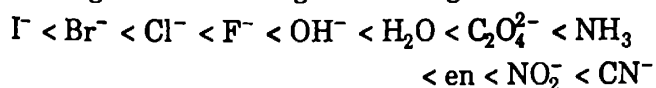
$$\Delta_t = -\frac{4}{9} \Delta_{oct}$$

In such cases, low spin configuration are rarely observed.



• The magnitude of  $\Delta_{oct}$  or  $\Delta_t$ , the orbitals splitting energy is decided by

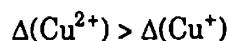
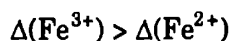
— **nature of the ligand** : which have been arranged in increasing field strength as:



— **geometry of the complex**:  $\Delta_t$  value (of tetrahedral complex) is about 50% compared to  $\Delta_{oct}$  value (of octahedral complexes)

— **nature of the metal ion**: going from Cr to W (through Mo),  $\Delta_{oct}$  increases 50% in each series change (i.e.,  $3d$  to  $4d$  to  $5d$ ). Thus, there is greater tendency of the second ( $4d$ ) and third ( $5d$ ) transition series to be low spin as compared to first ( $3d$ ) transition series.

— **oxidation state of the metal ion**



Thus, greater the ionic charge on the central metal ion, the greater the value of  $\Delta$ .

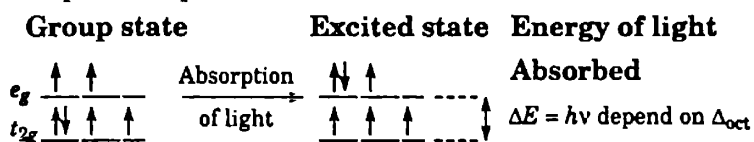
### Colour and the Spectrochemical Series

A substance appears coloured because it absorbs light that corresponds to one or more of the wavelengths in the visible region of the electromagnetic spectrum (4000 to 7000 Å) and transmits or reflects the other wavelengths. A combination of all wavelengths in the visible region is called "**white light**", sunlight is an example. The absence of all wavelengths in the visible region is blackness.

Most transition metal compounds are coloured. In transition metal compounds, the  $d$ -orbitals in any one energy level of the metal are not degenerate. They are often split into two sets of orbitals separated by energies,  $\Delta_{oct}$ , that correspond to wavelength of light in the visible region. The absorption of visible light causes electronic transition between orbitals in these sets. Colour of some transition metal nitrates in aqueous solutions are given below:

| Transition metal ion | Colour of aqueous solution |
|----------------------|----------------------------|
| $Cr^{3+}$            | Deep blue                  |
| $Mn^{2+}$            | Pale pink                  |
| $Fe^{2+}$            | Pale green                 |
| $Fe^{3+}$            | Orchid                     |
| $Co^{2+}$            | Pink                       |
| $Ni^{2+}$            | Green                      |
| $Cu^{2+}$            | Blue                       |

One transition of a high spin octahedral  $Co(III)$  complex is represented below :





The frequency ( $\nu$ ), and thus the wavelength and colour, of the light absorbed are related to  $\Delta_{\text{oct}}$ . This, in turn, depends on the crystal-field strength of the ligands. Hence, the colour and the visible absorption spectra of transition metal complexes, as well as their magnetic properties, provide information about the strengths of the ligand-metal interactions.

Table 18.9 gives the relationship among colours absorbed and colours transmitted or reflected in the visible region. The **spectral colour** is the colour associated with the wavelengths of the light absorbed by the sample. The **complimentary colour** is the colour associated with the wavelengths that are not absorbed by the sample, and is seen when the spectral colour is removed from white light. Complimentary colour of orange is spectral colour blue and *vice-versa* and is represented in the form of a wheel (to remember)

Table 18.9 Complimentary Colours

| Wavelength absorbed (Å) | Spectral colour (colour absorbed) | Complimentary colour (colour observed) |
|-------------------------|-----------------------------------|----------------------------------------|
| 4100                    | violet                            | lemon yellow                           |
| 4300                    | indigo                            | yellow                                 |
| 4800                    | blue                              | orange                                 |
| 5000                    | blue-green                        | red                                    |
| 5300                    | green                             | purple                                 |
| 5600                    | lemon yellow                      | violet                                 |
| 5800                    | yellow                            | indigo                                 |
| 6100                    | orange                            | blue                                   |
| 6800                    | red                               | blue-green                             |

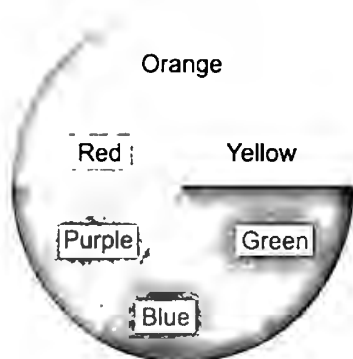
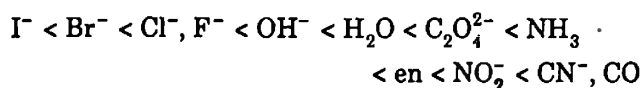


Fig. 18.1 Spectral colour and complimentary colour are opposite to each other

### DEEP Focus

- By study of visible spectra of many complexes, it is possible to arrange common ligands in order of increasing crystal field strength:



This arrangement is called the **spectrochemical series**.

- Strong field ligands, such as  $\text{CN}^-$ , usually produce **low spin** complexes, where possible, and **large crystal field-splittings**.
- Weak field ligands, such as  $\text{Cl}^-$ , usually produce **high spin** complexes and **small crystal field-splittings**. Low spin complexes usually absorb higher-energy (shorter-wavelength) light than do high spin complexes.
- In  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ , the Cr(III) is bonded to six  $\text{NH}_3$  ligands, which produce a relatively high value of  $\Delta_{\text{oct}}$ . This absorbs light in the blue and violet regions of visible light and thus orange-yellow complimentary colour is observed.
- $\text{H}_2\text{O}$  is a weaker field ligand than  $\text{NH}_3$ , hence,  

$$\Delta_{\text{oct}}([\text{Cr}(\text{H}_2\text{O})_6]^{3+}) < \Delta_{\text{oct}}([\text{Cr}(\text{NH}_3)_6]^{3+})$$
 and thus  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  absorbs lower-energy light and appears blue (complimentary colour)

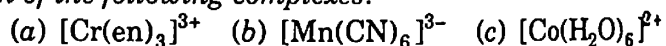
## Crystal Field Stabilisation Energy

Electrons in the  $t_{2g}$  orbitals of an octahedral complex are lower in energy, while electrons in  $e_g$  orbitals are higher in energy, than they would be in a spherical field. **The lower the total energy of a system, the more stable it is.**

The **crystal field stabilisation energy (CFSE)** of a complex is a measure of the net energy of stabilisation of a metal ion's electron's. CFSE is zero for weak field (high spin) octahedral  $d^0$ ,  $d^5$  and  $d^{10}$  complexes.

| Ion              | $d^n$    |          |
|------------------|----------|----------|
| $\text{Ca}^{2+}$ | $d^0$    | CFSE = 0 |
| $\text{Mn}^{2+}$ | $d^5$    |          |
| $\text{Zn}^{2+}$ | $d^{10}$ |          |

**Illustration 1** Draw a crystal field orbital energy level diagram, and predict the number of unpaired electrons for each of the following complexes:

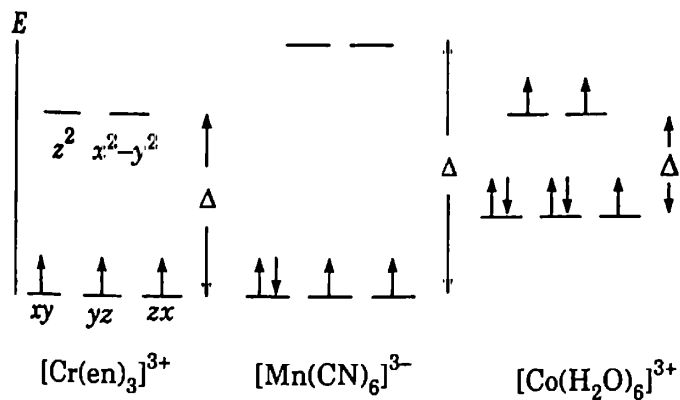


**Solution** (a)  $\text{Cr}^{3+}$  ( $[\text{Ar}]3d^3$ ) has three unpaired electrons. In the complex, they occupy the lower-energy set of  $d$ -orbitals.

(b)  $\text{Mn}^{3+}$  ( $[\text{Ar}]3d^4$ ) can have a high-spin or low-spin configuration. Because  $\text{CN}^-$  is a strong-field ligand, all four  $d$ -electrons go into the lower-energy  $d$ -orbitals. The complex is low-spin with two unpaired electrons.

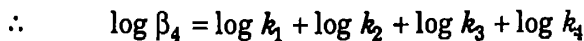
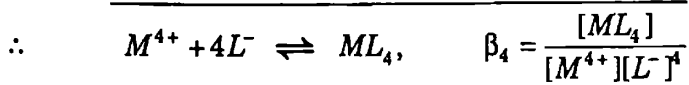
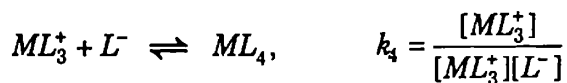
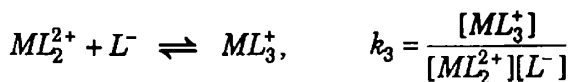
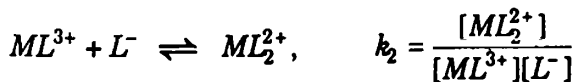
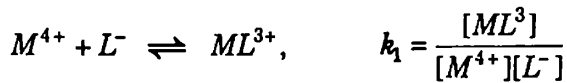
(c)  $\text{Co}^{2+}$  ( $[\text{Ar}]3d^7$ ) has a high-spin configuration with three unpaired electrons because  $\text{H}_2\text{O}$  is a weak-field ligand.

In the following orbital energy level diagrams, the relative values of the crystal field splitting  $\Delta$  are in accordance with the position of the ligands in the spectrochemical series ( $\text{H}_2\text{O} < \text{en} < \text{CN}^-$ ):

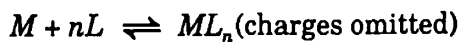


## Stability Constants and Stability of Coordination Compounds

Consider the stepwise formation of the complex  $ML_4$  from the metal ion  $M^{4+}$  (Lewis acid) and ligand  $L^-$  (Lewis base). Let  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$  be stepwise formation constants and  $\beta_4 (= k_f)$  be the overall formation constant. Thus,



If the complex is  $ML_n$ , and  $\beta_n$  the overall formation constant, then



$$\beta_n = \frac{[ML_n]}{[M][L]^n} = k_1 k_2 k_3 k_4 \dots k_n$$

$$\log \beta_n = \log k_1 + \log k_2 + \log k_3 + \dots + \log k_n$$

- $\beta_n$ , the stability constant, is related to thermodynamic stability when the system has reached equilibrium. Most of the measurements have been made from aqueous solutions, which means that when complex is formed, stronger ligand  $L$  (say  $\text{CN}^-$ , en) displaces weaker ligand  $\text{H}_2\text{O}$  of the aqua complex of the metal ion.



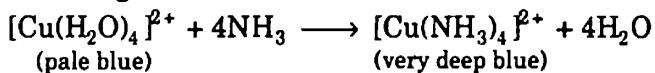
## DEEP Focus

- For a given ion and ligand, greater the charge on the metal ion, greater the stability. Thus, stability of  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-} > [\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$
- For the divalent ions of the first row transition elements (3d-series), the stabilities vary in the **Irving-Williams order**:  

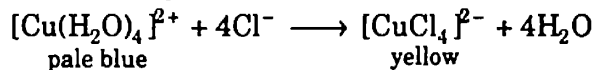
$$\text{Mn}^{\text{II}} < \text{Fe}^{\text{II}} < \text{Co}^{\text{II}} < \text{Ni}^{\text{II}} < \text{Cu}^{\text{II}} < \text{Zn}^{\text{II}}$$
- Ligands containing N, O or F donor atoms form most stable coordination compounds when metal ions are:
  - groups 1 and 2 elements, the inner transition elements and transition elements of groups 3 to 6 (Sc, Ti, V, Cr) called '**class a**' **acceptors**.
  - Transition elements — Rh, Pd, Ag, Ir, Au and Hg having relatively completely filled *d*-orbitals called '**class b**' **acceptors**.
  - The stability also depends on the formation of chelate rings and stabilisation due to chelation is called the **chelation effect**. This effect is maximum for the five and six-membered rings.
- If a multidentate ligand happens to be cyclic and there are no unfavourable steric effects, a further increase in stability occurs. This is termed the **macrocyclic effect**.

## Kinetic Consideration of Ligand Displacement

When we add  $\text{NH}_3(aq)$  to a solution containing  $\text{Cu}^{2+}$ , we observe a change in colour from pale blue to deep blue. The reaction involves  $\text{NH}_3$  molecules displacing  $\text{H}_2\text{O}$  molecules as ligands.



This reaction occurs very rapidly as rapidly as the two reactions can be brought together. The addition of  $\text{HCl}(aq)$  to an aqueous solution of  $\text{Cu}^{2+}$  produces an immediate colour change from pale blue to green, or even yellow if the  $\text{HCl}(aq)$  is sufficiently concentrated.

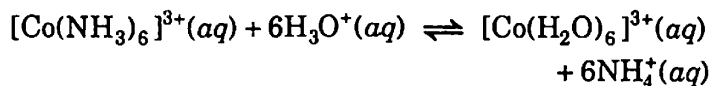


Complex ions in which ligands can be interchanged rapidly are said to be **labile**.  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , and  $[\text{CuCl}_4]^{2-}$  are all labile.

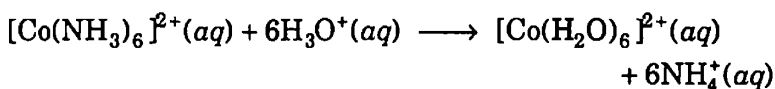
In freshly prepared  $\text{CrCl}_3(aq)$ ,  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$  produces a green colour, but colour gradually turns to violet. This colour change results from the very slow exchange of  $\text{H}_2\text{O}$  for  $\text{Cl}^-$  as ligands. A complex ion that exchanges ligands slowly is said to be **non-labile** or **inert**. In general, complex ions of the first transition series, except for those  $\text{Cr(III)}$  and  $\text{Co(III)}$  are kinetically labile. Those of the second and third transition series are generally kinetically inert.

These terms (labile/inert) are used to describe the different kinetics of the reactions that are thermodynamically allowed. Large activation energy barriers for ligand substitution reactions of inert

complexes make those reactions slow even though there may be thermodynamic tendency to proceed. In the substitution reaction

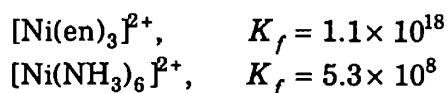


The products are favoured by an enormous amount, yet the inert  $[\text{Co}(\text{NH}_3)_6]^{3+}$  complex ion last for weeks in acidic solution because there is no low-energy pathway for the reaction. The cobalt (III) ion,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , is thermodynamically unstable relative to  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  but kinetically stable (inert). The closely related cobalt (II) complex,  $[\text{Co}(\text{NH}_3)_6]^{2+}$ , reacts with water in a matter of seconds.



The complex  $[\text{Co}(\text{NH}_3)_6]^{2+}$  is thermodynamically unstable and also kinetically labile.

**Illustration 1** Formation constant  $K_f$  for following complexes have been given :



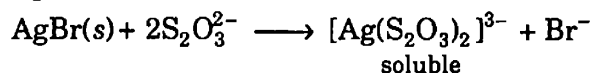
Explain the relative stability of these complexes.

**Solution** Ethylenediamine (en) is a bidentate ligand and ammine ( $\text{NH}_3$ ) is an unidentate ligand. Complex ion  $[\text{Ni}(\text{en})_3]^{2+}$  with multidentate ligand has much larger formation constant than do those with unidentate ligands. Thus,  $[\text{Ni}(\text{en})_3]^{2+}$  is more stable than  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ .

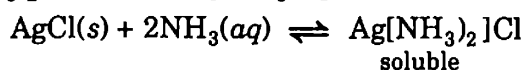
This additional stability of complex ions associated with chelate formation by multidentate ligands is known as the **chelation effect**.

## Applications of Coordination Chemistry

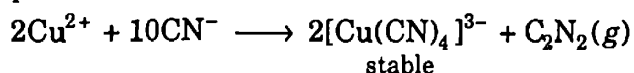
- The photographic "fixing" process removes unreacted  $\text{AgBr}$  which forms soluble complex with sodium thiosulphate:



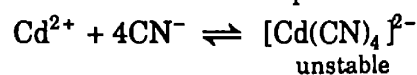
- In qualitative analysis of group I, there is formation of white precipitate of  $\text{AgCl}$ ,  $\text{Hg}_2\text{Cl}_2$ , and  $\text{PbCl}_2$ .  $\text{PbCl}_2$  is soluble in hot water.  $\text{AgCl}$  can be removed as soluble  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  on adding  $\text{NH}_3(\text{aq})$ :



In group II,  $\text{Cd}^{2+}$  can be precipitated as  $\text{CdS}$  in presence of  $\text{Cu}^{2+}$ . By treating the solution of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  with an excess of  $\text{CN}^-$ ,  $\text{Cu}^{2+}$  forms a stable complex in a redox reaction:

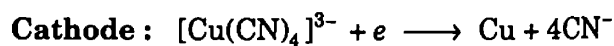


while  $\text{Cd}^{2+}$  forms less stable complex:



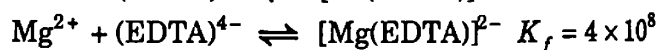
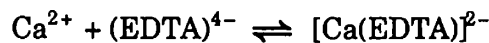
When  $\text{H}_2\text{S}$  gas is passed,  $[\text{Cd}(\text{CN})_4]^{2-}$  is precipitated as  $\text{CdS}$  without affecting  $[\text{Cu}(\text{CN})_4]^{3-}$  complex.

- Electrolyte solutions used in commercial electroplating are quite complex. A number of metals such as  $\text{Cu}$ ,  $\text{Ag}$  and  $\text{Au}$  are generally plated from solutions of their cyano complex ions. In the electrolysis reactions below the object to be plated is made the cathode and the piece of copper metal is the anode.



The net change simply involves the transfer of  $\text{Cu}$  metal from the anode to the cathode through the formation, migration and decomposition of complex ion  $[\text{Cu}(\text{CN})_4]^{3-}$ .

- Purification of water is also through complex formation. One method of water treatment involves **chelation**. Among the chelating agents widely employed are the salts of EDTA, usually the sodium salt. The formation constants of  $[\text{Ca}(\text{EDTA})]^{2-}$  and  $[\text{Mg}(\text{EDTA})]^{2-}$  are very large. Hence, on treating water with sodium salt of EDTA, concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  can be reduced to the point that these ions will not precipitate with soap or detergent.

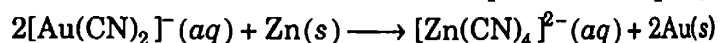
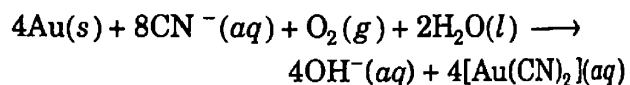


- Chelation with EDTA can also be used in the treatment of metal poisoning. If a person suffering from lead-poisoning is fed  $[\text{Ca}(\text{EDTA})]^{2-}$ , the following exchange occurs:

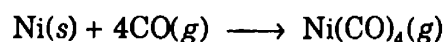


because  $K_f$  of  $[\text{Pb}(\text{EDTA})]^{2-}$  is  $1 \times 10^{18}$  and is thus more stable than  $[\text{Ca}(\text{EDTA})]^{2-}$ . The lead complex is excreted by the body and the  $\text{Ca}^{2+}$  remains as the body nutrient.

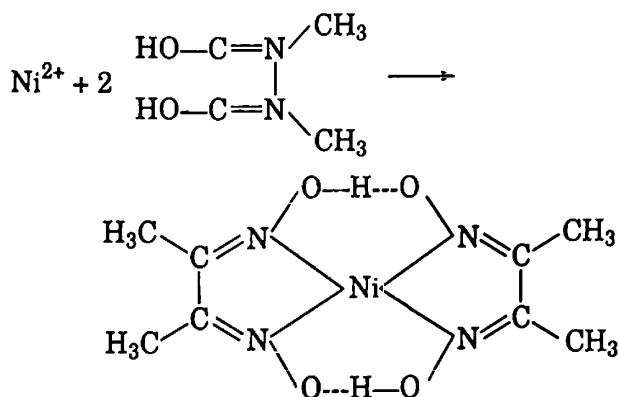
- The extraction of silver and gold involves the formation of cyanide complex:



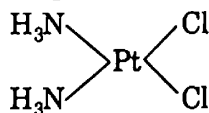
Mond's process involves formation of carbonyl complex of nickel:



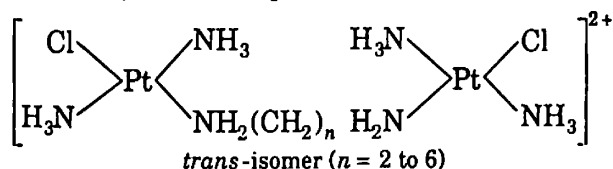
- Traces of  $\text{Ni}^{2+}$  salt can be detected by dimethyl glyoxime when cherry red precipitate of nickel-dimethyl glyoximate (chelate) is formed:



- *Cis*-diammine dichloroplatinum (II),  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ , is



one of a number of platinum coordination compounds used in the treatment of cancer. Commonly known as *cis-platin*, this compound has the ability to block the uncontrolled division of cancerous cells that results in the growth of tumours. Recent studies show that *cis-platin* can cause serious side effects, including severe kidney damage. It is being replaced by dinuclear platinum complex.



- Organometallic compound must contain, at least one metal-carbon bond.  $\text{Ni}(\text{CO})_4$  is also considered organometallic compound, though CO is not considered to be an organic compound. The suffix metallic often includes metalloids like boron, silicon, arsenic and tellurium as well as true metals. Metal-cyanides, though possessing an  $M-\text{C}$  bond are not included in organometallics.

#### • Main group organometallics

E.C. Frankland was the first chemist to synthesise an organometallic compound.

The *s*- and *p*-block organometallics are named according to substituent names used in organic chemistry.

|                            |                    |
|----------------------------|--------------------|
| $\text{CH}_3\text{Li}$     | methyl lithium     |
| $\text{B}(\text{CH}_3)_3$  | trimethyl boron    |
| $\text{Si}(\text{CH}_3)_4$ | tetramethyl silane |
| $\text{As}(\text{CH}_3)_3$ | trimethyl arsane   |

The oxidation number of the metallic element in an organometallic compound is based on the organic part being considered to be anionic. Thus,  $\text{CH}_3$  group in  $\text{Zn}(\text{CH}_3)_2$  has  $(-1)$  charge.

#### • *d*- and *f*-block organometallics

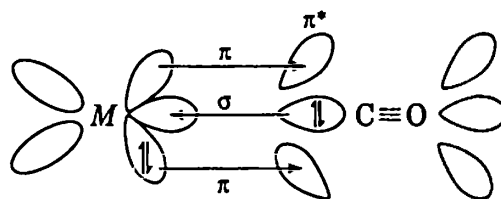
W.C. Zeise was the first to prepare organometallic compound of *d*-block. Examples are

- trichloroethene platinum (II) :  $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$
- tetracarbonyl nickel (0) :  $\text{Ni}(\text{CO})_4$
- bis(cyclopentadienyl) iron (II) :  $\text{Fe}(\text{C}_5\text{H}_5)_2$  also called ferrocene.

Ferrocene is stable in air, forms orange crystals and is diamagnetic. It is soluble in organic solvents (alcohol, ether and benzene) and insoluble in water, NaOH solution and conc. HCl solution.

It is thermally stable up to  $500^\circ\text{C}$ . The X-ray structure shows that this has a sandwich structure in which the metal atom is sandwiched between two planar cyclopentadienyl rings.

In metal carbonyls, CO as a ligand binds itself to metal atom through the carbon atom. It is a weak donor (a weak Lewis base) and forms a weak  $\sigma$ -bond to the central atom. CO is also an acceptor (Lewis acid) ligand and forms  $\pi$  bond to the metal. This characteristic property of back bonding stabilises the metal-ligand interaction.



## Target Practice 2

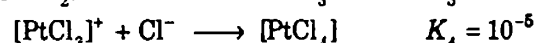
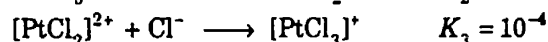
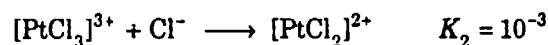
- The complex  $\text{CoCl}_4^{2-}$  has a tetrahedral structure.
  - How many *d*-electrons are on the cobalt? .....
  - What is its electronic configuration? .....
- Make complexes with varying  $\text{NH}_3$  ligands to satisfy primary and secondary valencies of platinum.
 

$\text{PtCl}_4 \cdot x\text{NH}_3$  .....

.....

.....

.....
- Arrange the complexes in (2) in increasing electrical conductivity .....
- What is CFSE of high-spin  $d^5$  complex of  $\text{Fe}^{3+}$ ? .....
- What is  $\text{pK}$  value of the complex  $[\text{PtCl}_4]^-$  if

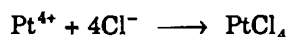


- Dilute equimolar solutions of each of the following compounds are prepared. Arrange the compounds in order of increasing molar conductivity (which is proportional to the number of ions) of these solutions :
  - $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$
  - $\text{K}[\text{Co}(\text{EDTA})]$
  - $[\text{Co}(\text{Py})_3(\text{CN})_3]$
  - $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
  - $[\text{Pt}(\text{NH}_3)_6]\text{Br}_4$
- While practice in the laboratory, you have some yellow spot of  $\text{FeCl}_3$  on your white shirt. Suggest a suitable reagent that can remove this yellow spot .....

## Answers

1. (a) 7  
 (b)  $t_{2g}(5) d_{xy}^2 d_{yz}^2 d_{zx}^2$   $\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow$   
 $e_g(2) d_{z^2}^1 d_{x^2-y^2}^1$   $\uparrow$   $\uparrow$

2. I.  $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$   
 II.  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$   
 III.  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$   
 IV.  $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$   
 V.  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$   
 3.  $\text{V} < \text{IV} < \text{III} < \text{II} < \text{I}$   
 4. Zero  
 5. On adding



$\therefore$  Overall stability constant

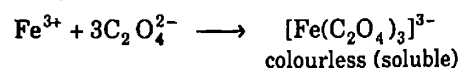
$$K = K_1 K_2 K_3 K_4 = 10^{-14}$$

$$\log K = \log K_1 + \log K_2 + \log K_3 + \log K_4 = -14$$

$$-\log K = 14$$

$$\text{p}K = 14$$

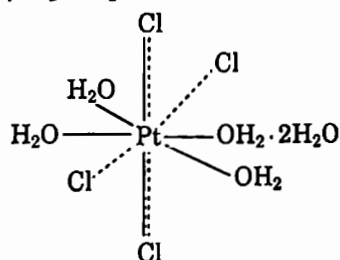
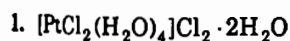
6. (c)  $<$  (b)  $<$  (d)  $<$  (a)  $<$  (e), ionisation being as:  
 (c) does not ionise  
 (b)  $\rightleftharpoons \text{K}^+ + [\text{Co}(\text{EDTA})]^-$  (two ions)  
 (d)  $\rightleftharpoons [\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+} + 2\text{Cl}^-$  (three ions)  
 (a)  $\rightleftharpoons 3\text{Na}^+ + [\text{Co}(\text{NO}_2)_6]^{3-}$  (four ions)  
 (e)  $\rightleftharpoons [\text{Pt}(\text{NH}_3)_6]^{4+} + 4\text{Br}^-$  (five ions)  
 7. Yellow spots can be removed by complexing  $\text{Fe}^{3+}$  by oxalate ion and washing it with water.



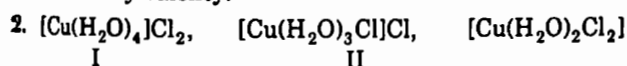
## Practice Exercise 2

- $\text{PtCl}_4 \cdot 6\text{H}_2\text{O}$  on reaction with  $\text{AgNO}_3$  forms 2 moles of  $\text{AgCl}$  (white ppt.) per mol of the  $\text{PtCl}_4 \cdot 6\text{H}_2\text{O}$ . What is complex? Give its Werner's representation.
  - $\text{CuCl}_2 \cdot x\text{H}_2\text{O}$  ( $x = 2, 3, 4$ ) can be represented by Werner's formula. What are those? Arrange them in increasing conducting power.
  - What are types of ions joined by primary valency and secondary valency of the metal in the following complexes?  
 (a)  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (b)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$   
 (c)  $\text{PtCl}_4 \cdot 6\text{NH}_3$  (d)  $\text{PtCl}_2 \cdot 2\text{H}_2\text{O}$
  - What is the true formula of the complex  $\text{PtCl}_4 \cdot 5\text{NH}_3$  if one mole of it on reaction with excess of  $\text{AgNO}_3$  yields three moles of white precipitate of  $\text{AgCl}$ ?
  - Write modern formulae of the following complexes based on the number of free  $\text{Cl}^-$  ions per formula unit:
- | Formula                                       | Colour      | $\text{Cl}^-$ ions in solution per formula unit |
|-----------------------------------------------|-------------|-------------------------------------------------|
| (a) $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ | violet      | 3                                               |
| (b) $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ | light green | 2                                               |
| (c) $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ | dark green  | 1                                               |
- Transition metal complexes containing,  $\text{CN}^-$  ligands are often yellow in colour, whereas those containing  $\text{H}_2\text{O}$  ligands are often green or blue. Explain.
  - The complex  $[\text{FeCl}_6]^{3-}$  is more paramagnetic than  $[\text{Fe}(\text{CN})_6]^{3-}$ . Explain.
  - Give a valence bond description of the bonding in each of the following complexes. Include orbital diagram for the free metal ion and the metal ion in the complex. Specify type of hybridisation and number of unpaired electrons.  
 (a)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  (b)  $[\text{NiBr}_4]^{2-}$   
 (c)  $[\text{Fe}(\text{CN})_6]^{3-}$  (d)  $[\text{MnCl}_6]^{3-}$
  - The absorption maximum for the complex ion  $[\text{Co}(\text{NH}_3)_6]^{3+}$  occurs at 470 nm.  
 (a) Predict the colour of the complex and  
 (b) Calculate the crystal field splitting in kJ/mol.
  - Draw a crystal field orbital energy level diagram, and predict the number of unpaired electrons for each of the following complexes:  
 (a)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  (b)  $[\text{Fe}(\text{CN})_6]^{4-}$   
 (c)  $(\text{VF}_6)^{3-}$
  - Explain why  $[\text{CoCl}_4]^{2-}$  (blue) and  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  (pink) have different colours? Which complex has its absorption bands at longer wavelength?
  - What is chelation effect?
  - Give the Irving —Williams order of stability of metal ions.
  - Stability constants of  $[\text{Cd}(\text{CN})_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are  $1.28 \times 10^{17}$  and  $1.0 \times 10^{31}$  respectively. Which is more stable?
  - Which of the following complexes is expected to be inert to the ligand substitution?  
 (a)  $[\text{Ni}(\text{en})_3]^{2+}$  (b)  $[\text{Mg}(\text{EDTA})]^{2-}$   
 (c)  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  (d)  $[\text{Co}(\text{NO}_2)_6]^{3-}$   
 (e)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  (f)  $[\text{Al}(\text{OH})_4]^-$   
 (g)  $[\text{FeF}_6]^{3-}$
  - Give the classification of organometallic compounds.
  - Discuss the nature of bonding in metal carbonyls.
  - Draw the structure of iron oxalate complex  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ . Describe the coordination geometry and identify any chelate ring. What is the oxidation number and the coordination number of iron?
  - What happens when  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is mixed with ethylenediamine in excess?

## Answers



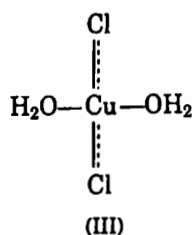
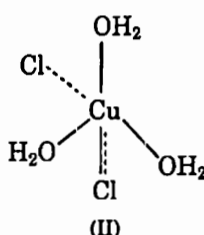
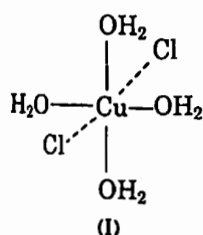
Since two moles of  $\text{AgCl}$  are obtained per mole of the compound hence, two  $\text{Cl}$  are joined by primary valency and two by secondary valency.



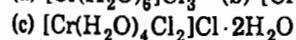
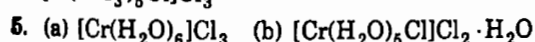
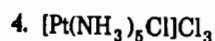
I

II

III

Conductance  $\text{III} < \text{II} < \text{I}$ 

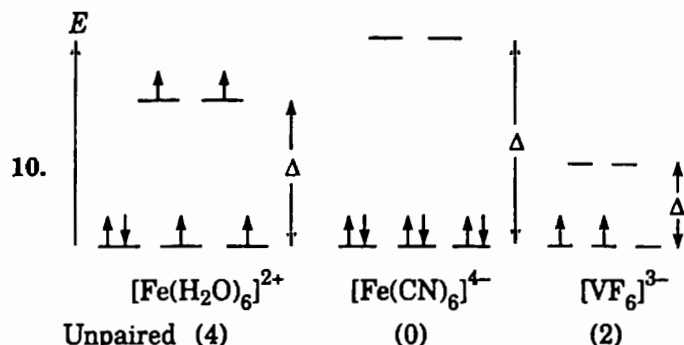
3. (a)  $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_3$ : Three  $\text{Cl}$  joined by primary valency (PV) and six  $\text{H}_2\text{O}$  joined by secondary valency (SV)
- (b)  $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ :  $\text{SO}_4^{2-}$  joined by (PV) and four  $\text{H}_2\text{O}$  by (SV)
- (c)  $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$ : Four  $\text{Cl}$  by (PV) and six  $\text{NH}_3$  by (SV)
- (d)  $[\text{Pt}(\text{H}_2\text{O})_2\text{Cl}_2]$ : Two  $\text{Cl}$  have dual nature joined by (PV) as well as (SV) while two  $\text{H}_2\text{O}$  by (SV).

6.  $\text{CN}^-$  is a strong ligand. Absorption near UV (blue), hence appear yellow.

7. Based on VBT,  $[\text{FeCl}_6]^{3-}$  has  $\text{Cl}^-$  as weak ligands,  $\text{Fe}$  is  $sp^3d^2$  hybridised (outer orbital complex) having five unpaired electrons.  $[\text{Fe}(\text{CN})_6]^{3-}$  has  $\text{CN}^-$  as strong ligand.  $\text{Fe}$  is  $d^2sp^3$  hybridised (inner orbital complex) having only one unpaired

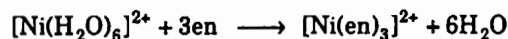
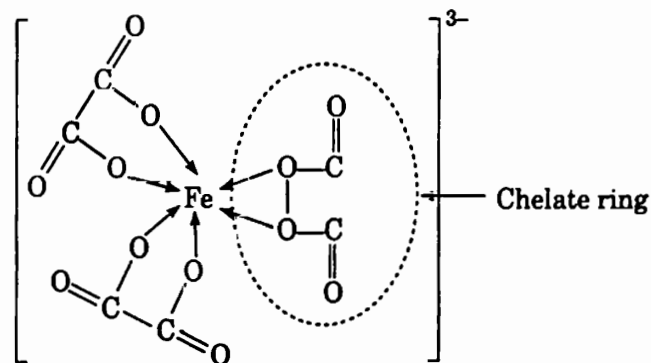
electron, hence,  $(\text{FeCl}_6)^{3-}$  is more paramagnetic than  $[\text{Fe}(\text{CN})_6]^{3-}$ . Also refer text.

8. Refer text

9. (a) orange (b)  $254.38 \text{ kJ mol}^{-1}$ 

electrons :

11.  $\Delta_{\text{tet}} < \Delta_{\text{oct}}$  hence, different colour  $[\text{CoCl}_4]^{2-}$  has absorption peak at higher wavelength.
12. Increase in stability due to presence of multidentate ligands (which causes ring formation) is called chelation effect.
13.  $\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} < \text{Zn}^{2+}$
14.  $[\text{Ni}(\text{CN})_4]^{2-}$
15. Only (d),  $[\text{Co}(\text{NO}_2)_6]^{3-}$ , due to very high value of formation constant.
16. Refer text
17. Refer text
18. Oxidation number of  $\text{Fe} = +3$   
Coordination number of  $\text{Fe} = 6$

19. Ethylenediamine (en) displaces  $\text{H}_2\text{O}$  forming a chelate.

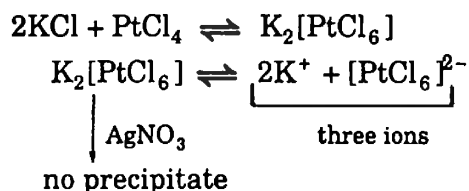
# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** The complex studied by Werner had a composition corresponding to the formula  $\text{PtCl}_4 \cdot 2\text{KCl}$ . From electrical-conductance measurements, he determined that each formula unit contained three ions. He also found that silver nitrate did not give a precipitate of  $\text{AgCl}$  with this complex. Write a formula for this complex that agrees with this information.

**Plan** Since  $\text{Ag}^+$  does not give precipitate with the complex, it means all the  $\text{Cl}$  are in coordinate sphere. Electrical conductance shows three ions per mol of complex, thus, formula can be derived.

**Solution** Given complex does not give precipitate with  $\text{AgNO}_3$ . It shows the absence of  $\text{Cl}^-$  ions. Thus, all the  $\text{Cl}$  ions are ligands and are in coordination sphere.



Thus, complex is  $\text{K}_2[\text{PtCl}_6]$

**Problem 2.** Write the structural formula corresponding to each of the following IUPAC names :

- hexaaquairon (II) chloride
- potassium tetrafluoroargentate (III)
- pentachlorotitanate (II) ion
- tetraamminedichlorocobalt (III) chloride
- dicyanoargentate (I) ion
- diamminetetrachloronickelate (II) ion
- tris (ethylenediamine) copper (II) sulphate
- sodium diaquatetrahydroxoaluminate (III)
- amminechlorobis (ethylene diamine) chromium (III) sulphate
- potassium tetracyanozincate (II)
- hexaamminechromium (III) tetrachlorocuprate (II)
- diamminedichloroplatinum (II)
- tetracarbonyl nickel (0)
- tetraammineplatinum (II) amminetrichloroplatinate (II)
- sodium bis(thiosulphato) argentate (I)
- potassium tetracyanonickelate (0)
- bis (cyclopentadienyl) iron (II)
- tetrathiocyanato-N-zincate (II) ion
- potassium tetraoxomanganate (VII)

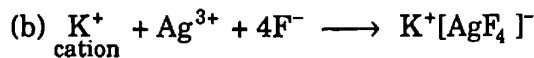
(t) potassium trisoxalatoaluminate (III)

(u) tetrapyridineplatinum (II) tetrachloroplatinate (II)

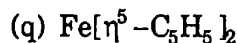
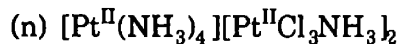
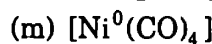
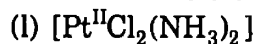
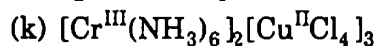
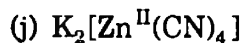
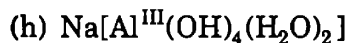
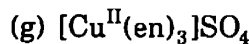
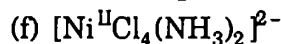
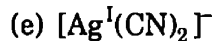
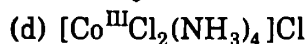
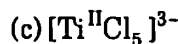
**Solution** (a)  $\text{Fe}^{2+} + 6\text{H}_2\text{O} + \text{Cl}^- \longrightarrow [\text{Fe}(\text{H}_2\text{O})_6]^{2+} \text{Cl}^-$   
Cation is a complex ion and carries + 2 charge, hence its structure is



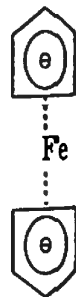
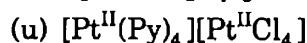
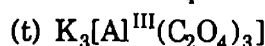
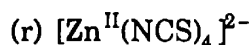
Oxidation state of the metal ion has been given in the structure. Students may omit it.



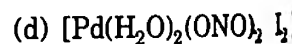
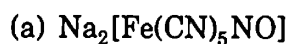
anion is a complex



$\eta^5$  means that all the five carbon atoms of cyclopentadienyl anion are coordinated to the metal ion.



**Problem 3.** Write IUPAC names of the following:



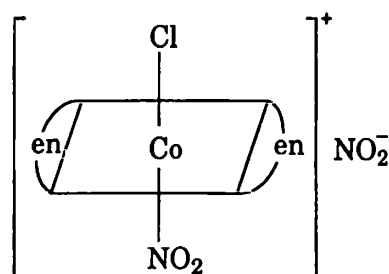
- (e)  $[\text{Co}(\text{NH}_3)_4(\text{NCS})\text{Cl}]^+$  (f)  $\text{K}_4[\text{FeO}_4]$   
 (g)  $\text{K}_2[\text{Co}(\text{N}_3)_4]$  (h)  $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$   
 (i)  $[\text{Cr}(\text{acac})_3]$  (j)  $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4][\text{PtCl}_2]$   
 (k)  $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$  (l)  $[\text{V}(\text{H}_2\text{O})_6]\text{Cl}_3$   
 (m)  $(\text{NH}_4)_3[\text{Co}(\text{C}_2\text{O}_4)_3]$   
 (n)  $\left[ (\text{NH}_3)_4\text{Co} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Co}(\text{en})_2 \right] \text{Cl}_4$   
 (o)  $\left[ (\text{en})_2\text{Co} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{Co}(\text{en})_2 \right]^{4+}$   
 (p)  $\text{Na}_2[\text{SiF}_6]$   
 (q)  $\text{K}_2[\text{CrO}_4]$   
 (r)  $[(\text{NH}_3)_5\text{Cr}-\text{OH}-\text{Cr}(\text{NH}_3)_5]\text{Cl}_5$   
 (s)  $[\text{Fe}(\text{en})_3][\text{Fe}(\text{CO})_4]$   
 (t)  $\text{TiCl}_4(\text{Et}_2\text{O})_2$   
 (u)  $\text{Mn}_2(\text{CO})_{10}$   
 (v)  $[\text{VO}(\text{acac})_2]$   
 (w)  $\text{Fe}[\text{Fe}(\text{CN})_6]^+$

- Solution** (a) Sodium pentacyanonitrosferrate (II)  
 (b) Bis (dimethylglyoximate) nickel (II)  
 (c) Ammonium tetrathiocyanatodinitrosochromate (III)  
 (d) Diaquadiiododinitritopalladium (IV)  
 (e) Tetraamminechloroisothiocyanatocobalt (III) ion  
 (f) Potassium tetraoxoferrate (IV)  
 (g) Potassium tetraazidocobalt (II) [ $\text{N}_3^-$  is azide]  
 (h) Dichlorobis(triphenyl phosphine) nickel (II)  
 (i) Tris (acetylacetonato)chromate (III)  
 [ $\text{acac}^-$  is  $\text{CH}_3\text{COCH}_2\text{CH}_2^-$ ]  
 (j) Tetrakis (pyridine)platinum (II) tetrachloroplatinate (II)  
 (k) Hexaammine cobalt (III) pentachlorocuprate (II)  
 (l) Hexaaquavanadium (III) chloride  
 (m) Ammonium tris(oxalato)cobaltate (III)  
 (n) Tetraamminebis (ethylenediamine)- $\mu$ -dihydroxo dicobalt (III) ion  
 (o) Tetrakis (ethylenediamine)- $\mu$ -hydroxo- $\mu$ -imidodichloro cobalt (III) ion  
 (p) Sodium hexafluorosilicate (IV)  
 (q) Potassium tetraoxochromate (VI)  
 (r)  $\mu$ -hydroxodecaamminedichromium (III) chloride  
 (s) Tris(ethylenediamine)iron (III) tetracarbonyl iron (III)  
 (metal in this complex can also be iron (II))  
 (t) Tetrachlorobis (diethyl ether) titanium (IV)  
 (u) Decacarbonyldiamanganese (0)  
 (v) Bis (acetylacetonato) oxovanadium (IV)  
 (w) Iron (III) hexacyanoferrate (II) ion  
 (also called Prussian blue)

**Problem 4.** A compound  $\text{Co}(\text{en})_2(\text{NO}_2)_2\text{Cl}$  has been prepared in a number of isomeric forms. One form undergoes no reaction with  $\text{AgNO}_3$  or (en) and is optically inactive. A second form reacts with  $\text{AgNO}_3$  but not with (en) and is optically inactive. A third form is optically active and reacts with both  $\text{AgNO}_3$  and (en). Identify each of these isomeric forms. Name and sketch each of the structures.

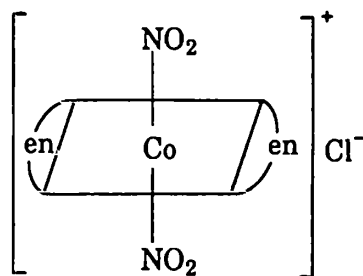
**Plan** Based on reactions with  $\text{AgNO}_3$  and (en), and optical activity, isomers can be identified.

**Solution First form :** There is no reaction with  $\text{AgNO}_3$ , hence no  $\text{Cl}^-$  ions outside coordination sphere. Also there is no reaction with bidentate (en), hence these ligands are *trans* to each other. Optical inactivity is also due to *trans* structure. Thus, it may have structure :



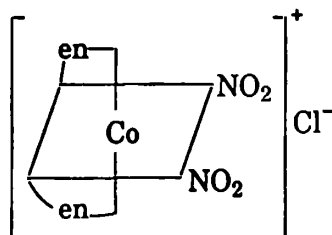
*trans*-chloronitrobis(ethylenediamine)cobalt (III) nitrite.

**Second form :** In this  $\text{Cl}^-$  is outside coordination sphere since it reacts with  $\text{AgNO}_3$ . As in the first form  $\text{NO}_2^-$  ligands are *trans* to each other being optically inactive. This is represented as,



*trans*-bis (ethylenediamine) dinitrocobalt (III) chloride

**Third form :** In this case also,  $\text{Cl}^-$  is outside coordination sphere. Also it shows reaction with (en) hence monodentate ligands are *cis* to each other. Being optically active, mirror image should not superimpose. Thus, it can have structure:



*cis*-bis (ethylenediamine) dinitrocobalt (III) chloride



**Problem 5.** Each of the compounds (a)  $\text{Pt}(\text{NH}_3)_6\text{Cl}_4$ , (b)  $\text{Cr}(\text{NH}_3)_6\text{Cl}_3$ , (c)  $\text{Co}(\text{NH}_3)_4\text{Cl}_3$  and (d)  $\text{K}_2\text{PtCl}_6$  has been dissolved in water to make its 0.001 M solution. Rank them in order of their increasing conductivity in solution (assume 100% ionisation in each case).

### Solution

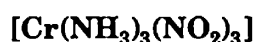
| Complex                                   | C.N. of metal ion | Actual presentation                              | Ionisation of complex                                   | Total ions |
|-------------------------------------------|-------------------|--------------------------------------------------|---------------------------------------------------------|------------|
| (a) $\text{Pt}(\text{NH}_3)_6\text{Cl}_4$ | 6                 | $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$          | $[\text{Pt}(\text{NH}_3)_6]^{4+} + 4\text{Cl}^-$        | 5          |
| (b) $\text{Cr}(\text{NH}_3)_6\text{Cl}_3$ | 6                 | $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$          | $[\text{Cr}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-$        | 4          |
| (c) $\text{Co}(\text{NH}_3)_4\text{Cl}_3$ | 6                 | $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ | $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{Cl}^-$ | 2          |
| (d) $\text{K}_2\text{PtCl}_6$             | 6                 | $\text{K}_2[\text{PtCl}_6]$                      | $2\text{K}^+ + [\text{PtCl}_6]^{2-}$                    | 3          |

Greater the number of ions, greater the conduction hence, order of increasing conductivity is (c) < (d) < (b) < (a)

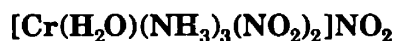
**Problem 6.** Two compounds have the empirical formula  $\text{Cr}(\text{NH}_3)_3(\text{NO}_2)_3$ . In aqueous solution, one of these conducts electricity while the other does not. Deduce their probable structures.

*Plan* Complex responsible for conductance ionises in aqueous solution. Hence, formula can be derived.

**Solution** We know C.N. of Cr is six, hence the complex that does not conduct electricity, would not ionise. Hence,  $\text{NO}_2^-$  and  $\text{NH}_3$  ligands are in coordination sphere and the complex is



The other complex that conducts electricity would ionise. Thus, in such complex  $\text{H}_2\text{O}$  should enter into coordination sphere making at least one  $\text{NO}_2^-$  available outside coordination sphere. This complex can be



**Problem 7.** A solution containing 2.665 g of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  is passed through a cation exchanger. The chloride ions obtained in solution react with  $\text{AgNO}_3$  and give 2.87 g of  $\text{AgCl}$ . Determine the structure of the compound (Cr = 52, Cl = 35.5, H = 1, O = 16, Ag = 108, N = 14)

*Plan* Free  $\text{Cl}^-$  after passing through the ion exchange gives white precipitate with  $\text{Ag}^+$ . From the given stoichiometric data, number of free  $\text{Cl}^-$  can be derived, hence the formula.

**Solution**  $\text{AgCl}$  is obtained only with free (ionisable) ions



*Plan* Based on C.N., their correct formulae are written and number of ions per mol of complex are determined. Conductivity is proportional to the number of ions.

$$\text{mole of AgCl obtained} = \frac{2.87}{143.5} = 0.02$$

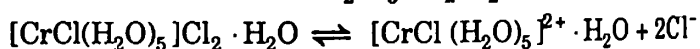
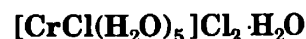
$$\text{mole of } \text{CrCl}_3 \cdot 6\text{H}_2\text{O} = \frac{2.665}{266.5} = 0.01$$

$$0.01 \text{ mole of complex gives} = 0.02 \text{ mol AgCl}$$

$$1 \text{ mole of complex gives} = 2 \text{ mol AgCl}$$

$$\text{Thus, numbers of free } \text{Cl}^- = 2$$

Also C.N. of Cr is six, hence complex is



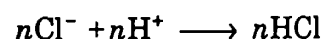
**Problem 8.** A solution containing 0.319 g of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  was passed through a cation exchange resin and acid coming out of the cation exchange resin required 28.5 mL of 0.125 M NaOH. Determine correct formula of the complex.

$$(\text{mol. wt. of the complex} = 266.5)$$

*Plan*  $\text{Cl}^- \equiv \text{HCl} \equiv \text{NaOH}$

From the number of moles of NaOH, number of moles of  $\text{Cl}^-$  are determined. Hence, complex is known.

**Solution** Let the number of  $\text{Cl}^-$  ions outside the coordination sphere or number of chloride ions which can be ionised be  $n$ . When the solution of the complex is passed through cation exchanger,  $n\text{Cl}^-$  ions will combine with  $\text{H}^+$  (of the cation exchanger) to form HCl



Thus, 1 mole of the complex will form  $n$  moles of HCl

$$1 \text{ mole of complex} \equiv n \text{ mol HCl} \equiv n \text{ moles NaOH}$$

$$\text{mole of the complex} = \frac{0.319}{266.5} = 0.0012 \text{ mol}$$

$$\text{mole of NaOH used} = \frac{28.5 \times 0.125}{1000} = 0.0036 \text{ mol}$$

0.0012 mol of complex  $\equiv$  0.0036 mol NaOH

$\equiv$  0.0036 mol HCl

$$1 \text{ mol of complex} \equiv \frac{0.0036}{0.0012} = 3 \text{ mol HCl}$$

$\therefore n = 3$

Thus, all the  $\text{Cl}^-$  ions are outside coordination sphere.

Hence, complex is  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ .

**Problem 9.** Metal carbonyls can have formula  $\text{M}(\text{CO})_x$  where  $x$  is the number of carbonyl units coordinated to metal  $M$ . If EAN of each metal in the carbonyl is 36, what are formulae of the carbonyl of Fe (26), Cr (24) and Ni (28) ?

**Plan** Based on EAN and atomic number, value of  $x$  in each complex is determined. Thus, their formulae are known.

**Solution** Carbonyl is neutral ligand, hence, oxidation number of  $M = 0$ . EAN of metal  $M$  (neutral) in the complex = 36. Each CO donates 2 electrons.

(i)  $\text{Fe}(\text{CO})_x$  EAN =  $Z - (\text{O.N.}) + 2x$

$$36 = 26 - 0 + 2x$$

$$x = 5$$

hence, complex is  $\text{Fe}(\text{CO})_5$

(ii)  $\text{Cr}(\text{CO})_x$   $Z = 24$

$$\text{EAN} = 36 = 24 - 0 + 2x$$

$$x = 6$$

hence, complex is  $\text{Cr}(\text{CO})_6$

(iii)  $\text{Ni}(\text{CO})_x$   $Z = 28$

$$\text{EAN} = 36 = 28 - 0 + 2x$$

$$x = 4$$

hence, complex is  $\text{Ni}(\text{CO})_4$

**Problem 10.** The EAN of each Mn ( $Z = 25$ ) in its carbonyl is 36. What is the structure of the carbonyl with molecular formula  $\text{Mn}_2(\text{CO})_{10}$  ?

**Plan** Based on EAN and  $Z$ , structure can be derived.

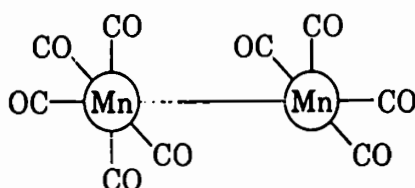
**Solution** Electrons from each Mn = 25

$$\text{Electrons from five CO ligands} = 2 \times 5 = 10$$

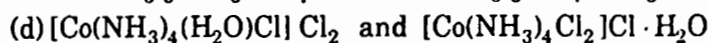
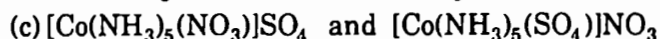
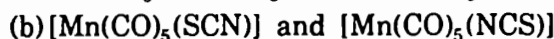
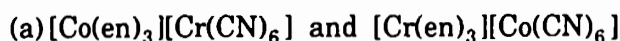
$$\text{Electron from (Mn—Mn) bond} = 1$$

Thus, EAN =  $25 + 10 + 1 = 36$

Thus, in the complex five CO (ligands) are coordinated to each Mn atom and sixth coordination number is attained by other Mn atom of (Mn—Mn) bond. Thus, it can have structure :



**Problem 11.** Give the name describing the type of structural isomerism displayed by each of the following pairs :



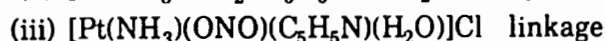
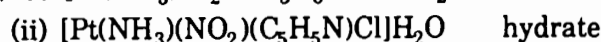
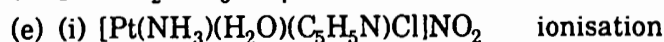
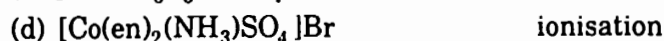
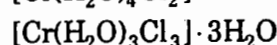
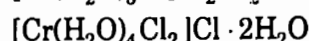
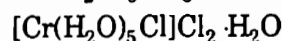
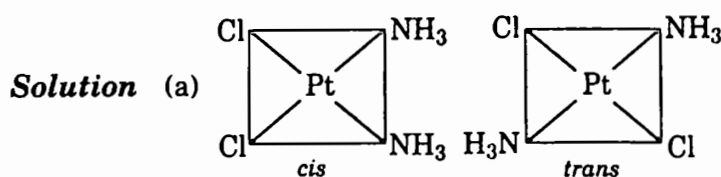
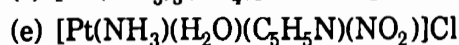
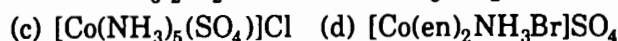
**Solution** (a) Coordination isomerism

(b) Linkage isomerism

(c) Ionisation isomerism

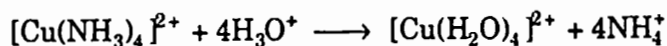
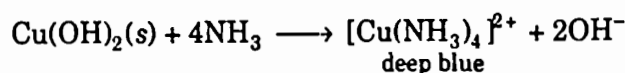
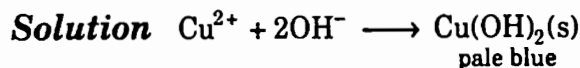
(d) Hydrate isomerism

**Problem 12.** Draw/write possible isomers of



**Problem 13.** Write equations to represent the following observation :

When NaOH is added to  $\text{CuSO}_4(\text{aq})$ , a pale blue precipitate forms. If  $\text{NH}_3(\text{aq})$  is added, the precipitate redissolves, producing a solution with an intense deep blue colour. If this deep blue solution is made acidic with  $\text{HNO}_3(\text{aq})$ , the colour is converted back to pale blue.



**Problem 14.** Write a series of equations to show the stepwise displacement of  $\text{H}_2\text{O}$  ligands in  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  by ethylenediamine (en), for which  $\log k_1 = 4.34$ ;  $\log k_2 = 3.31$  and  $\log k_3 = 2.05$ . What is the overall formation constant,  $\beta_3 (= k_f)$  for  $[\text{Fe}(\text{en})_3]^{3+}$  ?

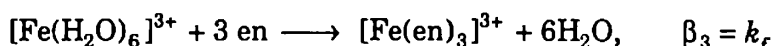
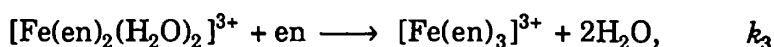
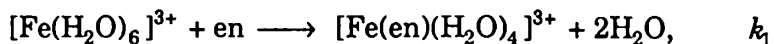
**Plan** If  $k_1$ ,  $k_2$  and  $k_3$  are stepwise formation constants and  $\beta_3$  is the overall formation constant, then

$$\beta_3 = k_1 k_2 k_3$$

$$\log \beta_3 = \log k_1 + \log k_2 + \log k_3$$

Thus,  $\beta_3$  can be calculated.

**Solution** Each ethylenediamine (en) being a bidentate ligand replaces two  $\text{H}_2\text{O}$  ligands (unidentate)



$$\text{Thus,} \quad \beta_3 = k_f = k_1 k_2 k_3$$

$$\therefore \log \beta_3 = \log k_1 + \log k_2 + \log k_3 \\ = 4.34 + 3.31 + 2.05 = 9.70$$

$$\therefore \beta_3 = 5.01 \times 10^9$$

Thus, overall formation constant is  $\beta_3 = k_f = 5.01 \times 10^9$

**Problem 15.** Oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) is sometimes used to clean rust stains from sinks and bathtubs. Explain the chemistry underlying this cleaning action.

**Plan** Rust is  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ . We are to study what happens to the rust when oxalic acid is used for cleaning.

**Solution** Oxalic acid forms a dark green coloured complex with rust stains ( $\text{Fe}^{3+}$  ions).



This complex is water soluble. Thus, rust stains can be removed by treating the fabric with oxalic acid and then washing with water.

**Problem 16.** Carbon monoxide (CO) is toxic when inhaled. Explain.

**Plan** We are to study the effect of CO on the internal body system.

**Solution** CO is toxic because it forms a complex with haemoglobin in the blood and this complex is more stable than oxy-haemoglobin. This prevents the haemoglobin in the red blood corpuscles from carrying oxygen round the body. This causes an oxygen deficiency, leading to unconsciousness and then death. The blood of victims of carbon monoxide poisoning is a brilliant red-pink colour rather than the dull red of normal blood.

# Master Exercises

## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

1. Which of the following complexes obey the rule of 18 (EAN rule)?

- (a)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $[\text{Cu}(\text{en})_3]^{2+}$ ,  $[\text{Cu}(\text{CN})_4]^{3-}$   
 (b)  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $\text{Fe}(\text{CO})_5$   
 (c)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $[\text{Ni}(\text{CO})_4]$   
 (d)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Cr}(\text{CO})_6]$   
 (e)  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{CoCl}_4]^{2-}$

2. Suppose 0.010 mole of each of the following compounds is dissolved (separately) in 1.0 L water :  $\text{KNO}_3$ ,  $[\text{Co}(\text{NH}_3)_6\text{Cl}_3]$ ,  $[\text{Cu}(\text{NH}_3)_2\text{Cl}_2]$ ,  $[\text{Na}_2(\text{PtCl}_6)]$

Rank the resulting four solutions in order of conductivity, from lowest to highest.

3. Predict which of the following octahedral complexes has the shortest  $\lambda_{\text{max}}$  :  $[\text{FeF}_6]^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ?

4. Is the coordination compound  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$  diamagnetic or paramagnetic.

5. Will methylamine  $[\text{CH}_3\text{NH}_2]$  be a monodentate or a bidentate ligand. With which of its atoms will it bind to a metal ion?

6. Consider following octahedral complexes

I :  $[\text{Fe}(\text{CN})_6]^{3-}$

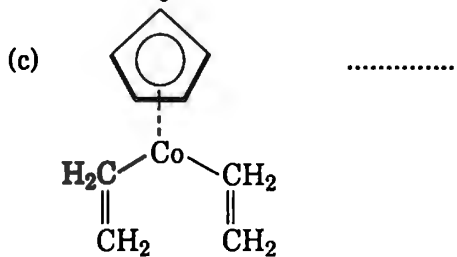
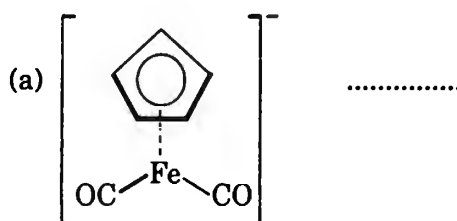
II :  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

- (a) Which has fewer unpaired electrons?  
 (b) How many unpaired electrons are present in each?  
 (c) What is CFSE in terms of  $\Delta_o$ ?

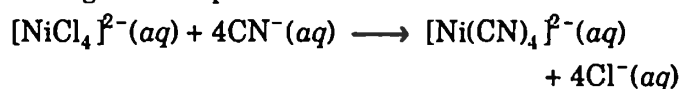
7. The chromium (III) ion in aqueous solution is blue-violet.

What is the complimentary colour to blue-violet?

8. Which of the following molecules/ions satisfies the EAN rule?



9. The anion  $[\text{NiCl}_4]^{2-}$  is paramagnetic, but when  $\text{CN}^-$  ions are added, the product  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic. Explain the observations.



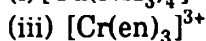
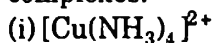
10. In water, the titanium (III) ion  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  has a broad absorption band at about 500 nm. What colour light is absorbed by the ion?

11. How many unpaired electrons expected for high spin and low-spin complexes of  $\text{Fe}^{2+}$ ?

### Analytical Questions

#### Coordination Number, Effective Atomic Number and Oxidation Number

1. Determine EAN of the metal ion in the following complexes:



2. What is coordination number and the oxidation state of the central metal ion in each of the following complexes?

- (a)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  (b)  $[\text{AlF}_6]^{3-}$   
 (c)  $[\text{Cu}(\text{CN})_4]^{2-}$  (d)  $[\text{Cr}(\text{NH}_3)_3\text{Br}_3]$   
 (e)  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$
3. Identify the ligands and give the coordination number for the central atom or ion in each of the following
- (a)  $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^-$  (b)  $\text{K}_4[\text{Fe}(\text{CN})_6]$   
 (c)  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  (d)  $[\text{Pd}(\text{NH}_3)_4]^{2+}$   
 (e)  $\text{Na}[\text{Au}(\text{CN})_2]$  (f)  $[\text{Co}(\text{en})_3]^{3+}$
4. Only two-third of the chlorine contained in the solution of the complex salt  $\text{CoCl}_3 \cdot 5\text{NH}_3$  were precipitated from it by silver nitrate. No cobalt or free ammonia were detected in the solution of the salt. The electrical conductivity of the solution shows that the salt dissociates into three ions. What is the coordination structure of the complex salt?
5. Silver nitrate precipitates the entire chlorine as silver chloride from a solution of the complex salt  $\text{PtCl}_4 \cdot 6\text{NH}_3$  and only one-fourth of the chlorine from a solution of the salt  $\text{PtCl}_4 \cdot 3\text{NH}_3$ . Write the coordination formulae of these salts, and determine the coordination number of the platinum in each case.
6. A sufficient amount of  $\text{AgNO}_3$  solution was added to a solution containing 23.35 g of the complex salt  $\text{CoCl}_3 \cdot 4\text{NH}_3$ . The mass of the precipitated  $\text{AgCl}$  was 14.35 g. Derive the coordination formula of the salt. ( $\text{Co} = 59 \text{ g mol}^{-1}$ )
7. Manganese carbonyl is a dimer,  $(\text{CO})_n\text{Mn}-\text{Mn}(\text{CO})_n$ . If each Mn atom has an EAN of 36, deduce the value of  $n$ , assuming single covalent bond between two Mn atoms.

## Nomenclature

8. Name the following:

- (a)  $[\text{Ag}(\text{NH}_3)_2]^+$  (b)  $[\text{Fe}(\text{H}_2\text{O})_3\text{OH}]^{2+}$   
 (c)  $[\text{ZnCl}_4]^{2-}$  (d)  $[\text{Pt}(\text{en})_2]^{2+}$   
 (e)  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]^+$  (f)  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$   
 (g)  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  (h)  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$   
 (i)  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$  (j)  $[\text{Co}(\text{en})_3]\text{Cl}_3$

9. Write IUPAC name of

- (a)  $[\text{Cr}(\text{NH}_3)_5\text{CO}_3]\text{Cl}$  (b)  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$   
 (c)  $\text{K}_3[\text{Cr}(\text{CN})_6]$  (d)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

10. Write the formulae of the following complexes:

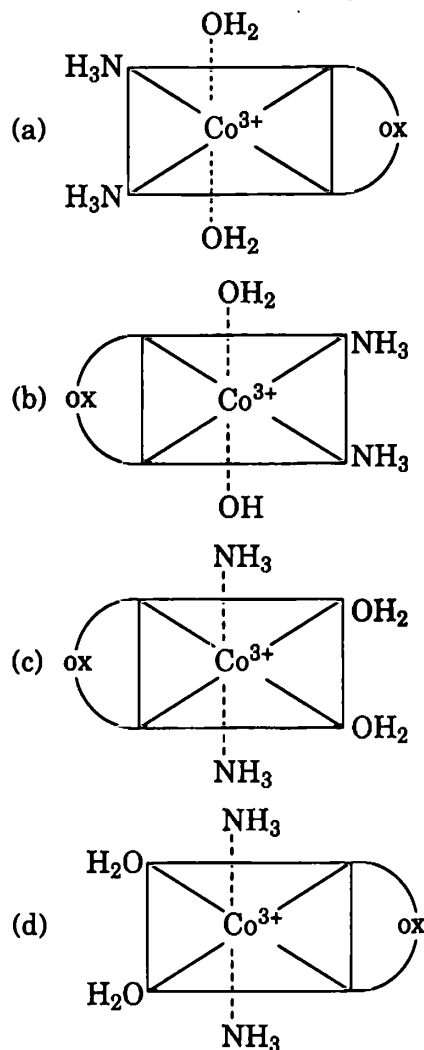
- (a) Pentamminechlorocobalt (III) ion  
 (b) Lithiumtetrahydroaluminate (III)

## Isomerism

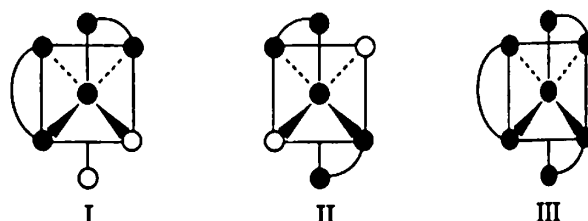
11. Draw the possible geometrical isomers for the following:

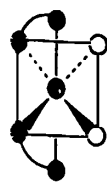
- (i)  $[\text{Pt}(\text{gly})_2]$  (ii)  $[\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)\text{Cl}_2]_2$

12. The complex ion;  $[\text{Pt}(\text{NH}_3)(\text{NH}_2\text{OH})(\text{NO}_2)(\text{Py})]^+$  has been found to be optically active. What is the probable geometry of the complex?
13. How many different structures are possible for each of the following complex ions?
- (a)  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  (b)  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$   
 (c)  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]^{3+}$  (d)  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{3+}$
14. Indicate what type of isomerism may be found in each of the following cases?
- (a)  $[\text{Zn}(\text{NH}_3)_4][\text{CuCl}_4]$  (b)  $[\text{Fe}(\text{CN})_5\text{SCN}]^{4-}$   
 (c)  $[\text{Ni}(\text{NH}_3)_5\text{Cl}]^+$  (d)  $[\text{Pt}(\text{Py})\text{Cl}_3]^-$   
 (e)  $[\text{Cr}(\text{NH}_3)_3(\text{OH})_3]^-$
15. The structure of four complex ions are given. Determine which, if any, of these complex ions are isomers (geometrical or optical); which, if any, are identical and which, if any, are distinctly different.

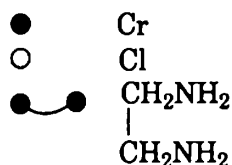


16. Consider the following ethylenediamine complexes





IV



- (a) Which complexes are chiral, and which are achiral?  
 (b) Draw the enantiomer of each chiral complex.  
 (c) Which, if any, of the chiral complexes are enantiomers of one another?

17. Which of the following complexes can exist as diastereoisomers?

- (a)  $[\text{Cr}(\text{NH}_3)_2\text{Cl}_4]^-$   
 (b)  $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$   
 (c)  $[\text{FeCl}_2(\text{NCS})_2]^{2-}$  (tetrahedral)  
 (d)  $[\text{PtCl}_2\text{Br}_2]^{2-}$  (square planar)

18. Two different compounds of Cr(III) have the same empirical formula,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ . One (A) is green and the other (B) is violet. (A) on reaction with excess  $\text{AgNO}_3$  gives 1 mole of  $\text{AgCl}$  per mol of (A) while (B) on reaction with excess  $\text{AgNO}_3$  gives 3 moles  $\text{AgCl}$  per mol of (B). Deduce formula of (A) and (B). What is affect of heating on each? Also compare their conductance.

19. A monomeric compound of cobalt gives the following data on quantitative analysis :

$\text{Co}^{3+}$  : 21.24%;  $\text{NH}_3$  : 24.77%,  $\text{Cl}^-$  : 12.81%;

$\text{SO}_4^{2-}$  : 34.65%;  $\text{H}_2\text{O}$  : 6.53%.

What is empirical formula of the complex ? Write possible isomers.

20. A, B and C are three complexes of chromium (III) with the empirical formula  $\text{H}_{12}\text{O}_6\text{Cl}_3\text{Cr}$ . All the three complexes have water and chloride ions as ligands. Complex A does not react with concentrated  $\text{H}_2\text{SO}_4$ , whereas complexes B and C lose 6.75% and 13.5% of their original weight, respectively, on treatment with concentrated  $\text{H}_2\text{SO}_4$ . Identify A, B and C.

## Bonding

21. A solution containing 1 g of the complex  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  was passed through a cation exchanger. The acid liberated was made up to 1 L. Calculate the strength of the acid formed.

22. The  $[\text{Ti}(\text{NCS})_6]^{3-}$  ion exhibits a single absorption band at 544 nm. Calculate the crystal field splitting energy  $\Delta$  (in  $\text{kJ mol}^{-1}$ ). Is  $\text{NCS}^-$  a stronger or weaker field ligand than water? Predict the colour of  $[\text{Ti}(\text{NCS})_6]^{3-}$ .

23. Predict

- (a) the number of unpaired electrons expected for the tetrahedral complex ion  $[\text{CoCl}_4]^{2-}$ ;

- (b) whether the square planar complex ion  $[\text{Cu}(\text{py})_4]^{2+}$  is diamagnetic or paramagnetic,  
 (c) whether the octahedral complex ion  $[\text{Mn}(\text{CN})_6]^{3-}$  or tetrahedral  $[\text{FeCl}_4]^-$  has the greater number of unpaired electrons.

24. Of the complex ions,  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Co}(\text{en})_3]^{3+}$ , one has a yellow colour in aqueous solution and the other blue. Match each ion with a expected colour and state your reason for doing so.

25. On the basis of the spectrochemical series, determine whether each of the following complexes is inner orbital or outer orbital and diamagnetic or paramagnetic.

- (a)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  (b)  $[\text{MnF}_6]^{3-}$   
 (c)  $[\text{Co}(\text{CN})_6]^{3-}$  (d)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$

26. Draw a crystal field energy level diagram, for each of the following complex ions and predict the number of unpaired electrons.

- (a)  $[\text{CrF}_6]^{3-}$  (b)  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$   
 (c)  $[\text{Fe}(\text{CN})_6]^{3-}$

27. The  $[\text{Fe}(\text{CN})_6]^{3-}$  ion has magnetic moment of 1.73 BM (Bohr Magneton) while  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  has a magnetic moment of 5.92 BM. Explain.

28. Among the following ions which has the highest paramagnetism?

- (a)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (b)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   
 (c)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  (d)  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$

29. Identify the complexes which are expected to be coloured, explain.

- (a)  $\text{Ti}(\text{NO}_3)_4$  (b)  $[\text{Cu}(\text{NCCH}_3)]^+\text{BF}_4^-$   
 (c)  $[\text{Cr}(\text{NH}_3)_6]^{3+}3\text{Cl}^-$  (d)  $\text{K}_3[\text{VF}_6]$

30. Select correct answer.

(I)  $\text{KF}$  combines with  $\text{HF}$  to form  $\text{KHF}_2$ . The compound contains the species :

- (a)  $\text{K}^+$ ,  $\text{F}^-$  and  $\text{H}^+$  (b)  $\text{K}^+$ ,  $\text{F}$  and  $\text{HF}$   
 (c)  $\text{K}^+$  and  $[\text{HF}_2]^-$  (d)  $[\text{KHF}]^+$  and  $\text{F}^-$

(II) Which compound is formed when excess of  $\text{KCN}$  is added to aqueous solution of copper sulphate?

- (a)  $\text{Cu}(\text{CN})_2$  (b)  $\text{K}_2[\text{Cu}(\text{CN})_4]$   
 (c)  $\text{K}[\text{Cu}(\text{CN})_2]$  (d)  $\text{K}_3[\text{Cu}(\text{CN})_4]$

31. In nitroprusside ion the iron and  $\text{NO}$  exist as  $\text{Fe}^{\text{II}}$  and  $\text{NO}^+$  rather than  $\text{Fe}^{\text{III}}$  and  $\text{NO}$ . These forms can be differentiated by

- (a) estimating the concentration of iron  
 (b) measuring the concentration of  $\text{CN}^-$   
 (c) measuring the solid state magnetic moment  
 (d) thermally decomposing the compound

32. Draw the structures of  $[\text{Co}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Ni}(\text{CO})_4]$ .

33. A metal complex having composition  $\text{Cr}(\text{NH}_3)_4\text{Cl}_2\text{Br}$  has been isolated in two forms (A) and (B). The form

(A) reacts with  $\text{AgNO}_3$  to give a white precipitate readily soluble in dilute aqueous ammonia, whereas (B) gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of (A) and (B) and state the hybridisation of chromium in each. Calculate their magnetic moments (spin-only value).

34. Deduce the structures of  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  considering hybridisation of the metal ion., Calculate the magnetic moment (spin only) of the species.

## Applications

35. Ethylenediamine tetraacetic acid, EDTA, in the form of its calcium salt, is administered as an antidote for lead poisoning. Explain why this reagent might be an effective medicine? Why is the calcium salt administered rather than the free acid?
36. Explain the following observations in terms of complex ion formation:
- $\text{Al}(\text{OH})_3$  is soluble in  $\text{NaOH}(\text{aq})$  but insoluble in  $\text{NH}_3(\text{aq})$ ;
  - $\text{ZnCO}_3(\text{s})$  is soluble in  $\text{NH}_3(\text{aq})$  but  $\text{ZnS}(\text{s})$  is not;
  - $\text{CoCl}_3$  is unstable in water solution, being reduced to  $\text{CoCl}_2$  and liberating  $\text{O}_2(\text{g})$ . On the other hand,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  can be easily maintained in aqueous solution.
37. Potassium alum,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  is obtained in the form of octahedral crystals when a solution of  $\text{K}_2\text{SO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  is concentrated by evaporation. Suggest specific experiments to specify whether it is a complex or double salt.

## NCERT Problems

- Complete the following statements for the coordination entity (complex ion)  $[\text{CrCl}_2(\text{OX})_2]^{3-}$ 
  - OX is abbreviation for .....
  - The oxidation number of chromium is .....
  - ..... is a bidentate ligand.
- Specify the oxidation numbers of the metals in the following coordination entities
  - $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{en})_2]^{2+}$
  - $[\text{PtCl}_4]^{2-}$
  - $[\text{CrCl}_3(\text{NH}_3)_3]$
  - $[\text{CoBr}_2(\text{en})_2]^+$
  - $\text{K}_3[\text{Fe}(\text{CN})_6]$
- Using IUPAC norms write the formulae for the following
  - Tetrahydroxozincate (II) ion
  - Hexaammine cobalt (III) sulphate
  - Potassiumtetrachloropalladate (II)
  - Potassium tris (oxalato) chromate (III)
  - Diamminedichloroplatinum (II)
  - Hexaammineplatinum (IV) ion
  - Potassium tetracyanonickelate (II)
  - Tetrabromocuprate (II) ion

- Pentaamminenitrito-O-cobalt (III) ion
- Pentaamminenitrito-N-cobalt (III) ion

- Using IUPAC norms write the systematic names of the following
  - $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
  - $[\text{CoCl}(\text{NO}_2)(\text{NH}_3)_4]\text{Cl}$
  - $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$
  - $[\text{PtCl}(\text{NH}_2\text{CH}_3)(\text{NH}_3)_2]\text{Cl}$
  - $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
  - $[\text{Co}(\text{en})_3]^{3+}$
  - $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
  - $[\text{NiCl}_4]^{2-}$
  - $[\text{Ni}(\text{CO})_4]$
- How many geometric isomers are possible in the following coordination entities?
  - $[\text{Cr}(\text{OX})_3]^{3-}$
  - $[\text{CoCl}_3(\text{NH}_3)_3]$
- Draw the structures of optical isomers of
  - $[\text{Cr}(\text{OX})_3]^{3-}$
  - $[\text{PtCl}_2(\text{en})_2]^{2+}$
  - $[\text{CrCl}_2(\text{en})(\text{NH}_3)_2]^+$
- Draw all the isomers (geometric and optical) of
  - $[\text{CoCl}_2(\text{en})_2]^+$
  - $[\text{CoCl}(\text{en})_2(\text{NH}_3)]^{2+}$
  - $[\text{CoCl}_2(\text{en})(\text{NH}_3)_2]^+$
- Draw the structure of
  - Cis*-dichlorotetracyano-chromate (III)
  - Mer*-triamminetrichlorocobalt (III)
  - Fac*-triaquatrininitro-N-cobalt (III)
- Write the correct formulae for the following coordination compounds
  - $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (violet, with 3 chloride ions/unit formula)
  - $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (light green colour, with 2 chloride ions/unit formula)
  - $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (dark green colour, with 1 chloride ion/unit formula)

[Hints : Some of these compounds may exist as hydrates].
- Aqueous copper sulphate solution (blue in colour) gives
  - a green precipitate with aqueous potassium fluoride, and
  - a bright green solution with aqueous potassium chloride.

Explain these experimental results.
- Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory
  - $[\text{Fe}(\text{CN})_6]^{4-}$
  - $[\text{FeF}_6]^{3-}$
  - $[\text{Co}(\text{OX})_3]^{3-}$
  - $[\text{CoF}_6]^{3-}$
- Write the valence bond description of
  - $[\text{Ni}(\text{CN})_4]^{3-}$
  - $[\text{NiCl}_4]^{2-}$

13. Write the formulae of the following

- methyllithium
- tetramethylsilane
- trimethylbismuth
- trimethylarsane

(e) hexamethyldialuminium

(f) trimethylboron

14. Give IUPAC name and draw the structure of

- $\text{Ni}(\text{CO})_4$
- $\text{Fe}(\text{CO})_5$
- $[\text{PtCl}_3(\text{C}_2\text{H}_2)]^-$
- $[\text{Cr}(\text{CO})_6]$

## Exercise 2

### (Stage 2 : High Skill Problem Solving)

#### Only One Option Correct

1. A compound has the empirical formula  $\text{CoCl}_3 \cdot 5\text{NH}_3$ .

When an aqueous solution of this compound is mixed with excess silver nitrate, 2 moles of  $\text{AgCl}$  precipitate per mol of compound. On reaction with excess  $\text{HCl}$ , no  $\text{NH}_4^+$  is detected. Hence, it is

- $[\text{Co}(\text{NH}_3)_5\text{Cl}_2]\text{Cl}$
- $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
- $[\text{Co}(\text{NH}_3)_5\text{Cl}_3]$
- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{NH}_3$

2. In the above compound in (Q. 1),

- all the Cl show primary valency (PV)
- two Cl show (PV) and one Cl secondary valency (SV)
- two Cl show (PV) and one Cl (PV) as well as (SV)
- all the Cl show (SV)

3. If there is 100% ionisation of this complex in (Q. 1) above, its 1 M solution at 300 K will have osmotic pressure equal to

- 8.21 atm
- 24.63 atm
- 49.28 atm
- 73.89 atm

4. Why is  $[\text{Ni}(\text{en})_3]^{2+}$ , nearly  $10^{10}$  times more stable than  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ?

- $\text{NH}_3$  evaporates easily and causes instability to  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  complex
- Six  $\text{NH}_3$  ligands cause steric hindrance around the  $\text{Ni}^{2+}$  centre
- 'en' is a chelating ligand and forms thermodynamically more stable complexes
- $\text{NH}_3$  is the weakest ligand known

5. Which of the following complexes is diamagnetic?

- $[\text{Fe}(\text{CN})_6]^{4-}$
- $[\text{Cu}(\text{NH}_3)_4]^{2+}$
- $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
- $[\text{Ni}(\text{en})_2]^{2+}$

6. Which of the following cations is not paramagnetic?

- $\text{Sc}^{3+}(\text{aq})$
- $\text{Ti}^{3+}(\text{aq})$
- $\text{V}^{3+}(\text{aq})$
- $\text{Cr}^{3+}(\text{aq})$

7. Which of the following complexes is not a chelate?

- bis (dimethylglyoximate) nickel (II)
- potassium ethylenediamine tetrathiocyanato chromate (III)
- tetrammine carbonatocobalt (III) nitrate
- trans*-diglycinatoplatinum (II)

8. Which of the following complexes exhibit optical isomerism?

- trans*-tetramminedithiocyanatocobalt(III) ion
- cis*-diamminedicarbonatocobalt (III) ion
- trans*-diamminedicarbonatocobalt (III) ion
- cis*-glycinatoplatinum (II)

9. What is the ratio of uncomplexed to complexed  $\text{Zn}^{2+}$  ion in a solution that is 10 M in  $\text{NH}_3$ , if the stability constant of  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  is  $3 \times 10^9$ ?

- $3.3 \times 10^{-9}$
- $3.3 \times 10^{-11}$
- $3.3 \times 10^{-14}$
- $3 \times 10^{-13}$

10. The formula of a carbonyl complex of cobalt,  $(\text{CO})_n\text{Co}-\text{Co}(\text{CO})_n$ , in which there a single covalent Co—Co bond is

- $\text{Co}_2(\text{CO})_4$
- $\text{Co}_2(\text{CO})_6$
- $\text{Co}_2(\text{CO})_8$
- $\text{Co}_2(\text{CO})_{10}$

11. If excess of  $\text{AgNO}_3$  solution is added to 100 mL of a 0.024 M solution of dichlorobis (ethylene diamine) cobalt (III) chloride. How many moles of  $\text{AgCl}$  be precipitated?

- 0.0012
- 0.0016
- 0.0024
- 0.0048

12. Among  $\text{Ni}(\text{CO})_4$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $\text{NiCl}_4^{2-}$

- $\text{Ni}(\text{CO})_4$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $\text{NiCl}_4^{2-}$  is paramagnetic
- $\text{Ni}(\text{CO})_4$  and  $\text{NiCl}_4^{2-}$  are diamagnetic and  $[\text{Ni}(\text{CN})_4]^{2-}$  is paramagnetic
- $\text{Ni}(\text{CO})_4$  is diamagnetic and  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $\text{NiCl}_4^{2-}$  are paramagnetic
- $\text{NiCl}_4^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $\text{Ni}(\text{CO})_4$  is paramagnetic

13.  $[\text{Cr}(\text{NH}_3)_5\text{Br}]\text{Cl}$  and  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Br}$  can be distinguished by/and isomerism shown is

- $\text{BaCl}_2$ , ionisation
- $\text{AgNO}_3$ , ionisation
- $\text{AgNO}_3$ , coordinate
- $\text{BaCl}_2$ , linkage

14. Which is true for  $[\text{Ni}(\text{en})_2]^{2+}$ ,  $Z(\text{Ni}) = 28$ ?

- Paramagnetism,  $dsp^2$ , square planar, C.N. of Ni = 2
- Diamagnetism,  $dsp^2$ , square planar, C.N. of Ni = 4



- (c) Diamagnetism,  $sp^3$ , tetrahedral, C.N. of Ni = 4  
 (d) Paramagnetism,  $sp^3$ , square planar, C.N. of Ni = 4
15. Which is Prussian blue?  
 (a)  $KFe^{III}[Fe^{II}(CN)_6]$  (b)  $KFe^{III}[Fe^{III}(CN)_6]$   
 (c)  $K_2[Fe^{II}(CN)_6]$  (d)  $K_3[Fe(CN)_6]$
16.  $[Ni(CN)_4]^{2-}$  and  $[NiCl_4]^{2-}$  have similarity but not in  
 (a) magnetic moment (b) C.N. and O.N.  
 (c) structure (d) both (a) and (c)
17. Which has maximum EAN of the underlined atoms?  
 (Cr = 24, Co = 27, Fe = 26, Ni = 28)  
 (a)  $[Cr(EDTA)]^-$  (b)  $[Co(en)_3]^{3+}$   
 (c)  $[Fe(C_2O_4)_3]^{3-}$  (d)  $[Ni(CN)_4]^{2-}$
18. Oxidation number of Cr in the following complex is  

$$\left[ (H_2O)_6Cr \begin{array}{c} \diagup O_2 \diagdown \\ \diagdown O-O \diagup \end{array} Cr(H_2O)_6 \right]^{3+}$$
  
 (a) 3 (b) 6  
 (c) 4 (d) 5
19. Which has maximum coordinating (donor) points?  
 (a) DMG (b) EDTA  
 (c) en (d) py
20. Following ligands can show linkage isomerism  
 (a) CNS (b)  $NO_2$   
 (c) CN (d) all of these
21.  $[Fe^{II}(O_2)(CN)_4Cl]^{4-}$  is named as  
 (a) chlorotetracyanodioxoferrate (II) ion  
 (b) chlorotetracyanoperoxoferate (II) ion  
 (c) chlorotetracyanosuperoxoferate (II) ion  
 (d) none of the above is correct
22. Which has maximum conductance?  
 (a)  $PtCl_4 \cdot 6NH_3$  (b)  $PtCl_4 \cdot 5NH_3$   
 (c)  $PtCl_4 \cdot 4NH_3$  (d) Equal
23. Primary and secondary valency of Pt in  $[Pt(en)_2Cl_2]Cl_2$  are  
 (a) 4, 4 (b) 4, 6  
 (c) 6, 6 (d) 4, 4
24. Which is used in cancer-chemotherapy?  
 (a) *Cis*-platin (b) Zeisse's salt  
 (c) Both (a) and (b) (d) None of these
25. Which one of the following complex species does not obey the EAN rule?  
 (a)  $[Cu(CN)_4]^{3-}$  (b)  $[Cr(NH_3)_6]^{3+}$   
 (c)  $[Fe(CN)_6]^{4-}$  (d)  $[Ni(CO)_4]$
26. Which has aromatic ring in complex?  
 (a) DMG in dimethyl glyoximate  
 (b) Cyclopenta-dienyl anion in ferrocene  
 (c) Both (a) and (b)  
 (d) None of the above
27. Extraction of Ag from sulphide ore and removal of unreacted silver from photographic plate involve complexes  
 (a)  $[Ag(S_2O_3)_2]^{3-}$  in both  
 (b)  $[Ag(CN)_2]^-$  in both  
 (c)  $[Ag(S_2O_3)_2]^{3-}$ ,  $[Ag(CN)_2]^-$   
 (d)  $[Ag(CN)_2]^-$ ,  $[Ag(S_2O_3)_2]^{3-}$
28.  $[Co(NH_3)_5(NO_2)]^{2+}$  and  $[Co(NH_3)_5(ONO)]^{2+}$  will differ in  
 (a) colour (b) structure  
 (c) hybridisation (d) magnetic moment
29. In which case racemic mixture is obtained on mixing its mirror images in 1 : 1 molar ratio?  
 (a)  $[Cr(en)_3]^{3+}$  (b)  $[Ni(DMG)_2]$   
 (c) *Cis*- $[Cu(Gly)_2]$  (d) In all cases
30. EAN of the elements (\*) are equal in  
 (a)  $Ni(CO)_4$ ,  $[Fe(CN)_6]^{4-}$   
 (b)  $[Ni(en)_2]^{2+}$ ,  $[Fe(H_2O)_6]^{2+}$   
 (c)  $[Co(CN)_6]^{3-}$ ,  $[Fe(CN)_6]^{3-}$   
 (d)  $[Ni(en)_2]^{2+}$ ,  $[Sc(H_2O)_6]^{3+}$
31. Consider the following complexes:  
 (1)  $K_2PtCl_6$  (2)  $PtCl_4 \cdot 2NH_3$   
 (3)  $PtCl_4 \cdot 3NH_3$  (4)  $PtCl_4 \cdot 5NH_3$   
 Their electrical conductances in aqueous solutions are  
 (a) 256, 0, 97, 404 (b) 404, 0, 97, 256  
 (c) 256, 97, 0, 404 (d) 404, 97, 256, 0
32. Which one of the following is an example of coordination isomerism?  
 (a)  $[Co(NH_3)_5Br]SO_4$  and  $[Co(NH_3)_5SO_4]Br$   
 (b)  $[Co(NH_3)_5NO_2]Cl_2$  and  $[Co(NH_3)_5ONO]Cl_2$   
 (c)  $[Cr(H_2O)_6]Cl_3$  and  $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$   
 (d)  $[Cr(NH_3)_6][Co(CN)_6]$  and  $[Co(NH_3)_6][Cr(CN)_6]$
33. Which of the following compounds show optical isomerism?  
 I. *Cis*- $[Co(NH_3)_4Cl_2]^+$  II. *Trans*- $[Co(en)_2Cl_2]^+$   
 III. *Cis*- $[Co(en)_2Cl_2]^+$  IV.  $[Co(en)_3]^{3+}$   
 Select the correct answer using the codes given below  
 (a) I and II (b) II and III  
 (c) III and IV (d) I, III and IV
34. Lead poisoning in the body can be removed by  
 (a) EDTA in the form of calcium dihydrogen salt  
 (b) *cis*-platin  
 (c) Zeisse's salt  
 (d) DMG
35.  $[Pt(NH_3)(NO_2)Py(NH_2OH)]^+$  will form geometrical isomers  
 (a) 2 (b) 3  
 (c) 4 (d) 5

36. The coordination number of Pt in the complex ion  $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$  is  
 (a) 3 (b) 4  
 (c) 5 (d) 6

37. Of the following complex ions one exhibits optical isomerism. That one is

- (a)  $\text{cis}-[\text{Co}(\text{en})_2\text{Cl}_2]^+$  (b)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$   
 (c)  $[\text{Co}(\text{NH}_3)_2\text{Cl}_4]^-$  (d)  $\text{trans}-[\text{Co}(\text{en})_2\text{Cl}_2]^+$

38. Of the following complex ions, one exhibits isomerism. That is

- (a)  $[\text{Ag}(\text{NH}_3)_2]^+$  (b)  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$   
 (c)  $[\text{Pt}(\text{en})\text{Cl}_2]$  (d)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$

39. The number of unpaired electrons expected for the complex ion  $[\text{Cr}(\text{NH}_3)_6]^{2+}$  is

- (a) 2 (b) 3  
 (c) 4 (d) 5

40. Of the following complex ions, one is a Bronsted-Lowry acid. That one is

- (a)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  (b)  $[\text{FeCl}_4]^-$   
 (c)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  (d)  $[\text{Zn}(\text{OH})_4]^{2-}$

41. Of the following complex ions, the one that probably has the largest overall formation constant,  $K_f$ , is

- (a)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (b)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$   
 (c)  $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{3+}$  (d)  $[\text{Co}(\text{en})_3]^{3+}$

42. When concentrated HCl is added to a solution of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  ion, an intense blue colour develops due to the formation of which one of the following?

- (a)  $[\text{CoCl}_6]^{4-}$  (b)  $[\text{CoCl}_4]^{2-}$   
 (c)  $[\text{CoCl}_2(\text{H}_2\text{O})_4]$  (d)  $[\text{CoCl}(\text{H}_2\text{O})_5]^+$

43. Select the correct statement.

- (a) Complex ion  $[\text{MoCl}_6]^{3-}$  is paramagnetic  
 (b) Complex ion  $[\text{Co}(\text{en})_3]^{3+}$  is diamagnetic  
 (c) Both (a) and (b) are correct  
 (d) None of the above is correct

44. Match the geometry (given in column A) with the complexes (given in column B) in

| Geometry : A       | Complex : B                         |
|--------------------|-------------------------------------|
| I : Octahedral     | P : $[\text{Ni}(\text{CN})_4]^{2-}$ |
| II : Square planar | Q : $\text{Ni}(\text{CO})_4$        |
| III : Tetrahedral  | R : $[\text{Fe}(\text{CN})_6]^{4-}$ |

- |       |    |     |       |    |     |
|-------|----|-----|-------|----|-----|
| I     | II | III | I     | II | III |
| (a) P | Q  | R   | (b) R | P  | Q   |
| (c) R | Q  | P   | (d) Q | P  | R   |

45. The complex  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  is formed in the brown ring test for nitrates when freshly prepared  $\text{FeSO}_4$  solution is added to aqueous solution of  $\text{NO}_3^-$  followed by addition of conc.  $\text{H}_2\text{SO}_4$ . Select correct statement about this complex.

- (a) Colour change is due to charge transfer  
 (b) It has iron in +1 oxidate state and nitrosyl as  $\text{NO}^+$

- (c) It has magnetic moment of 3.87 BM confirming three unpaired electrons in Fe  
 (d) All the above are correct statements

46. While  $\text{Ti}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$  afford a large number of tetrahedral complexes,  $\text{Cr}^{3+}$  never does this, the reason being

- (a)  $\text{Cr}^{3+}$  forces high crystal field splitting with a varieties of ligands  
 (b) crystal field stabilisation energy in octahedral *vis-a-vis* tetrahedral  $\text{Cr}^{3+}$  system plays the deciding role  
 (c) the ionic radius of  $\text{Cr}^{3+}$  is the largest among the other  $M^{3+}$  ions mentioned  
 (d) electronegativity of  $\text{Cr}^{3+}$  is the largest among these trivalent 3d-metals and so chromium prefers to be associated with as many ligands as its ionic radius permits

47. Isomerisms exhibited by  $[\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2]^+$  are

- (a) ionisation, optical  
 (b) hydrate, optical  
 (c) geometrical, optical  
 (d) coordinate, geometrical

48. The crystal field-splitting for  $\text{Cr}^{3+}$  ion in octahedral field increases for ligands  $\text{I}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CN}^-$  and the order is

- (a)  $\text{I}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{CN}^-$   
 (b)  $\text{CN}^- < \text{I}^- < \text{H}_2\text{O} < \text{NH}_3$   
 (c)  $\text{CN}^- < \text{NH}_3 < \text{H}_2\text{O} < \text{I}^-$   
 (d)  $\text{NH}_3 < \text{H}_2\text{O} < \text{I}^- < \text{CN}^-$

49. Which of the following types of bonds are present in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ?

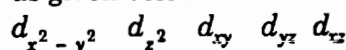
I : Electrovalent    II : Covalent    III : Coordinate  
 Select correct answer out of

- (a) I, II (b) II, III  
 (c) I, III (d) I, II, III

50. Arrange the following in order of decreasing number of unpaired electrons:

- I :  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$     II :  $[\text{Fe}(\text{CN})_6]^{3-}$   
 III :  $[\text{Fe}(\text{CN})_6]^{4-}$     IV :  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$   
 (a) IV, I, II, III (b) I, II, III, IV  
 (c) III, II, I, IV (d) II, III, I, IV

51. In an octahedral complex, if ligands on one axis are displaced little away from their ideal positions, the crystal field splitting of d-orbitals for this complex is as given below



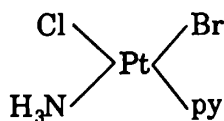
The ligands are displaced on which axis/ axes

- (a) x- and y (b) y-only  
 (c) x-only (d) z-only

52. Which one of the following compounds has tetrahedral geometry?

- (a)  $[\text{Ni}(\text{CN})_4]^{2-}$  (b)  $[\text{NiCl}_4]^{2-}$   
 (c)  $[\text{PdCl}_4]^{2-}$  (d)  $[\text{Pd}(\text{CN})_4]^{2-}$

53. Aqueous Fe(III) ion develops intense red colour with  $\text{SCN}^-$  while Fe(II) does not. It is due to  
 (a) Fe(III) ion forms a charge transfer complex with  $\text{SCN}^-$  ions  
 (b) Fe(III) is reduced to Fe(I) which is deep red in colour  
 (c)  $\text{SCN}^-$  ion oxidises to  $\text{CN}^-$  ion that form red complex with Fe(III) ion  
 (d)  $\text{SCN}^-$  ion does not form any complex with Fe(II) ion
54. The intense blue colour of Prussian blue salts arises from which one of the following?  
 (a)  $d-d$  transition  
 (b) inter valence electron transfer  
 (c) ligand to metal charge transfer  
 (d) metal to ligand charge transfer
55. Which one of the following is the correct order of the wavelengths of absorption for complexes?  
 I :  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  II :  $[\text{Ni}(\text{NH}_3)_6]^{2+}$   
 III :  $[\text{Ni}(\text{NO}_2)_6]^{4-}$   
 (a)  $\text{I} > \text{II} > \text{III}$  (b)  $\text{II} > \text{I} > \text{III}$   
 (c)  $\text{III} > \text{II} > \text{I}$  (d)  $\text{III} > \text{I} > \text{II}$
56. What are the spin-only magnetic moments (in BM) for Ni(II) ion in square-planar and octahedral geometry, respectively?  
 (a) 0, 2.83 (b) 2.83, 2.83  
 (c) 2.83, 0 (d) 0, 0
57. What is CFSE of a free Co(II) ion on forming the tetrahedral chloro complex  $[\text{CoCl}_4]^{2-}$  (in the units of  $\Delta_o$ )?  
 (a) 0.6 (b) 1.2  
 (c) 1.8 (d) 2.4
58. Which one of the following complexes is expected to have lowest  $\Delta_o$  values?  
 (a)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (b)  $[\text{CoF}_6]^{3-}$   
 (c)  $[\text{Rh}(\text{NH}_3)_5]^{3+}$  (d)  $[\text{Ir}(\text{NH}_3)_6]^{3+}$
59. If  $\Delta_o$  and  $\Delta_t$  represent crystal field splitting energies for  $d$ -orbitals for octahedral and tetrahedral geometries respectively, then for  $d^6$  (high spin in both cases), what are CFSE (ignore the pairing energy) respectively?  
 (a)  $0.6 \Delta_o$  and  $0.6 \Delta_t$  (b)  $0.4 \Delta_o$  and  $0.4 \Delta_t$   
 (c)  $0.4 \Delta_o$  and  $0.6 \Delta_t$  (d)  $0.6 \Delta_o$  and  $0.4 \Delta_t$
60. The complex  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$  and  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$  are called  
 (a) ionisation isomer (b) linkage isomers  
 (c) coordination isomer (d) geometrical isomer
61. The complex



can be formally formed from  $\text{K}_2[\text{PtCl}_4]$  by which one of the following sequences of substitution of the chloride ions?

- (a) Py,  $\text{Br}^-$ ,  $\text{NH}_3$  (b)  $\text{Br}^-$ , Py,  $\text{NH}_3$   
 (c)  $\text{Br}^-$ ,  $\text{NH}_3$ , Py (d)  $\text{NH}_3$ ,  $\text{Br}^-$ , Py
62. Consider the following statements in respect of  $[\text{CoCl}_6]^{4-}$  complex ion  
 I : It is paramagnetic  
 II : It is low-spin complex  
 III : Oxidation number of cobalt is -4  
 IV : The coordination number of cobalt is 6  
 Select correct statements.  
 (a) all of the above (b) III and IV only  
 (c) I and IV only (d) I and II only
63. The reaction between metallic silver and aqueous NaCN forming a soluble complex occurs in the presence of  
 (a) nitrogen (b) helium  
 (c) argon (d) oxygen
64. What type of isomerism is present in the pair of complexes  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ ?  
 (a) Linkage isomerism (b) Ligand isomerism  
 (c) Ionisation isomerism (d) Coordination isomerism

## One or More Than One Options Correct

- Which are correct statements?  
 (a)  $[\text{Ag}(\text{NH}_3)_2]^+$  is linear with  $sp$  hybridised  $\text{Ag}^+$  ion  
 (b)  $\text{NiCl}_4^{2-}$ ,  $\text{VO}_4^{3-}$  and  $\text{MnO}_4^-$  have tetrahedral geometry  
 (c)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  have  $dsp^2$  hybridisation of the metal ion  
 (d)  $\text{Fe}(\text{CO})_5$  have bipyramidal structure with  $dsp^3$  hybridised iron
- Which of the following are paramagnetic?  
 (a)  $[\text{Ni}(\text{CN})_4]^{2-}$  (b)  $[\text{NiCl}_4]^{2-}$   
 (c)  $[\text{CoF}_6]^{3-}$  (d)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- Which of the following can show coordination isomerism?  
 (a)  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$   
 (b)  $[\text{Fe}(\text{NH}_3)_6]_2[\text{Pt}(\text{CN})_6]_3$   
 (c)  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{C}_2\text{O}_4)_3]$   
 (d)  $[\text{Pt}(\text{en})_3](\text{SO}_4)_2$
- 0.0012 mole of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  was passed through cation exchange resin and acid coming out of it required 28.5 mL of 0.125 M NaOH. Hence, complex is  
 (a)  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (b)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$   
 (c)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (d)  $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$
- Which is/are correct statement(s)?  
 (a)  $[\text{Co}(\text{en})_3][\text{Cr}(\text{CN})_6]$  will display coordination isomerism  
 (b)  $[\text{Mn}(\text{CO})_5(\text{SCN})]$  will display linkage isomerism  
 (c)  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]\text{SO}_4$  will display ionisation isomerism  
 (d) None of the above is correct

6. Identify the complexes which is/are expected to be coloured

- (a)  $\text{Ti}(\text{NO}_3)_4$  (b)  $[\text{Cu}(\text{NCCH}_3)]^+\text{BF}_4^-$   
(c)  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  (d)  $\text{K}_3[\text{VF}_6]$

7. Nitroprusside ion is

A :  $[\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}]^+ \text{ and not}$

B :  $[\text{Fe}^{\text{III}}(\text{CO})_5\text{NO}]^+ \text{ A and B can be differentiated by}$

- (a) estimating the concentration of iron  
(b) measuring the concentration of  $\text{CN}^-$   
(c) measuring the magnetic moment  
(d) thermally decomposing the compound

8. The effective atomic number of  $\text{Co}(\text{CO})_4$  is 35 and hence, is less stable. It attains stability by

- (a) oxidation of Co (b) reduction of Co  
(c) dimerization (d) tetramerization

9. Bidentate ligands are

- (a)  $\text{C}_2\text{O}_4^{2-}$  (oxalate)  
(b) en (ethylenediamine)  
(c) DMG (dimethyl glyoxime)  
(d) Gly (glycine)

10. Which of the following complexes are chelates?

- (a) bis-(dimethyl glyoximate) nickel (II)  
(b) Potassium ethylenediaminetetracyanato chromate (III)  
(c) Tetraamminedicyanocobalt (III) nitrate  
(d) trans-diglycinatopalladium (II)

11.  $\text{CN}^-$  is a strong field ligand. This is due to the fact that

- (a) it carries negative charge  
(b) it is a conjugate base of weak acid  
(c) it can accept electrons from metal species  
(d) it forms high spin complexes with metal species

12. Considering  $\text{H}_2\text{O}$  as a weak field ligand, the number of unpaired electrons in  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  will be (At. no. of Mn = 25)

- (a) three (b) five  
(c) two (d) four

13. Which of the following coordination compounds would exhibit optical isomerism?

- (a) Pentaamminenitrocobalt(III) iodide  
(b) Diamminedichloroplatinum(II)  
(c) Trans-dicyanobis (ethylenediamine) chromium(III) chloride  
(d) Tris-(ethylenediamine) cobalt(III) bromide

14. In which of the following compounds transition metal may have zero oxidation state?

- (a)  $[\text{Fe}(\text{CO})_5]$  (b)  $[\text{Ni}(\text{CN})_4]^{2-}$   
(c)  $\text{Fe}_2\text{O}_3$  (d)  $\text{CrO}_5$

15. Which one of the following complexes will have four different isomers?

- (a)  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$   
(b)  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]\text{Cl}$   
(c)  $[\text{Co}(\text{PPh}_3)_2(\text{NH}_3)\text{Cl}_2]\text{Cl}$   
(d)  $[\text{Co}(\text{en})_3]\text{Cl}_3$

## Passage Comprehension Questions

### Passage 1

Three different compounds (A, B and C) are known to have the empirical formula  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}(X)$

When exposed to a dehydrating agent

A loses 2 moles of water per mole of the compound (X).

B loses 1 mole of water and compounds C loses no water. Answer the following questions.

1. Thus, A, B and C are

- | A                                                                                     | B                                                                                | C                                                                                 |
|---------------------------------------------------------------------------------------|----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|
| (a) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ | $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ | $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$                                    |
| (b) $[\text{Cr}(\text{H}_2\text{O})_2\text{Cl}_3] \cdot 4\text{H}_2\text{O}$          | $[\text{Cr}(\text{H}_2\text{O})\text{Cl}_3] \cdot 5\text{H}_2\text{O}$           | $[\text{CrCl}_3] \cdot 6\text{H}_2\text{O}$                                       |
| (c) $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$          | $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$         | $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$                                    |
| (d) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$                                    | $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ | $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ |

2. Which is most conducting in aqueous solution?

- (a) A (b) B  
(c) C (d) Equal

3. One mole each of A, B and C is treated with excess of  $\text{AgNO}_3$ . There is formation of white precipitate of  $\text{AgCl}$ .

Moles of white precipitates are

- | A     | B | C |
|-------|---|---|
| (a) 1 | 2 | 3 |
| (b) 3 | 2 | 1 |
| (c) 1 | 3 | 2 |
| (d) 3 | 1 | 2 |

### Passage 2

The octahedral complex ions  $[\text{FeCl}_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  are both paramagnetic but the former is high spin and the latter is low spin.

Based on the above study, answer the following questions

1. High spin complex  $[\text{FeCl}_6]^{3-}$  has the d-configuration as

- (a)  $t_{2g}^3 e_g^2$  (b)  $t_{2g}^5$   
(c)  $t_{2g}^2 e_g^3$  (d)  $e_g^5$

2. Low spin complex  $[\text{Fe}(\text{CN})_6]^{3-}$  has the d-configuration as

- (a)  $t_{2g}^3 e_g^2$  (b)  $t_{2g}^5$   
(c)  $t_{2g}^2 e_g^3$  (d)  $e_g^5$

3. Unpaired electrons in  $[\text{FeCl}_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  are respectively

- (a) 5, 2 (b) 5, 1  
(c) 3, 2 (d) 2, 3

4. CFSE for the complexes are

| $[\text{FeCl}_6]^{3-}$ | $[\text{Fe}(\text{CN})_6]^{3-}$ |
|------------------------|---------------------------------|
| (a) 0                  | 0                               |
| (b) $-2\Delta_o$       | 0                               |
| (c) 0                  | $-2\Delta_o$                    |
| (d) $-2\Delta_o$       | $-2\Delta_o$                    |

### Passage 3

The Alsatian-Swiss chemist Alfred Werner pioneered the field of coordination chemistry in the late nineteenth century. At that time, a number of compounds of cobalt (III) chloride with ammonia were known, with general formulae



Treatment of these compounds with aqueous HCl acid did not remove the ammonia. However treatment of the compounds with excess of  $\text{AgNO}_3$  at 273 K gave white precipitate of AgCl in varying ratio depending on the structure. Also each complex had electrical conductivity of varying nature. Based on the above study, answer the following questions.

1. Which complex has the maximum electrical conductivity?

- |                                        |                                        |
|----------------------------------------|----------------------------------------|
| (a) $\text{CoCl}_3 \cdot 3\text{NH}_3$ | (b) $\text{CoCl}_3 \cdot 4\text{NH}_3$ |
| (c) $\text{CoCl}_3 \cdot 5\text{NH}_3$ | (d) $\text{CoCl}_3 \cdot 6\text{NH}_3$ |

2. There is no reaction of the compound with aqueous HCl indicating that there is no free  $\text{NH}_3$ . Thus,  $\text{NH}_3$  ligand is bonded to cobalt (III) by

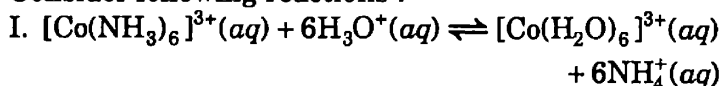
- |                     |                       |
|---------------------|-----------------------|
| (a) primary valency | (b) secondary valency |
| (c) both of these   | (d) None of these     |

3. One mole of the compound gave three moles of white precipitate of AgCl, on reaction with aqueous  $\text{AgNO}_3$ . Thus, complex is

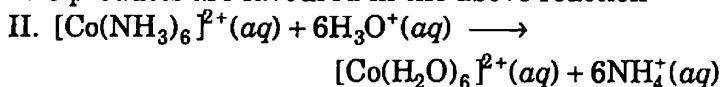
- |                                        |                                        |
|----------------------------------------|----------------------------------------|
| (a) $\text{CoCl}_3 \cdot 4\text{NH}_3$ | (b) $\text{CoCl}_3 \cdot 5\text{NH}_3$ |
| (c) $\text{CoCl}_3 \cdot 6\text{NH}_3$ | (d) all of these                       |

### Passage 4

Consider following reactions :



The products are favoured in the above reaction



This, reactions (II) takes place with  $\text{H}_2\text{O}$  in a matter of seconds

Based on the above reactions, answer the following questions.

1. Select correct statement.

- |                                                                                                                                                 |
|-------------------------------------------------------------------------------------------------------------------------------------------------|
| (a) $[\text{Co}(\text{NH}_3)_6]^{3+}$ is thermodynamically and kinetically stable relative to $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$          |
| (b) $[\text{Co}(\text{NH}_3)_6]^{3+}$ is thermodynamically unstable but kinetically stable relative to $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ |

- |                                                                                                                                                 |
|-------------------------------------------------------------------------------------------------------------------------------------------------|
| (c) $[\text{Co}(\text{NH}_3)_6]^{3+}$ is thermodynamically and kinetically unstable relative to $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$        |
| (d) $[\text{Co}(\text{NH}_3)_6]^{3+}$ is thermodynamically stable but kinetically unstable relative to $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ |

2. Which is true in terms of  $\Delta G^\circ$ ?

- |                                                         |
|---------------------------------------------------------|
| (a) $\Delta G_I^\circ$ is more negative than that of II |
| (b) $\Delta G_I^\circ$ is less negative than that of II |
| (c) $\Delta G_I^\circ = \Delta G_{II}^\circ < 0$        |
| (d) $\Delta G_I^\circ = \Delta G_{II}^\circ > 0$        |

3. Which is thermodynamically unstable and also kinetically labile?

- |                                              |                                              |
|----------------------------------------------|----------------------------------------------|
| (a) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ | (b) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ |
| (c) $[\text{Co}(\text{NH}_3)_6]^{3+}$        | (d) $[\text{Co}(\text{NH}_3)_6]^{2+}$        |

### Passage 5

The octahedral complex ion  $[\text{FeCl}_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  are both paramagnetic. Answer the following questions.

1. Select correct statements.

- |                                                                                                 |
|-------------------------------------------------------------------------------------------------|
| (a) $[\text{FeCl}_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ both are high-spin complex       |
| (b) $[\text{FeCl}_6]^{3-}$ is high-spin and $[\text{Fe}(\text{CN})_6]^{3-}$ is low-spin complex |
| (c) $[\text{FeCl}_6]^{3-}$ is low-spin and $[\text{Fe}(\text{CN})_6]^{3-}$ is high-spin complex |
| (d) $[\text{FeCl}_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ both are low-spin complexes      |

2.  $[\text{FeCl}_6]^{3-}$  has

- |                                                   |
|---------------------------------------------------|
| (a) five unpaired electrons ( $t_{2g}^3 e_g^2$ )  |
| (b) one unpaired electron ( $t_{2g}^1$ )          |
| (c) three unpaired electrons ( $t_{2g}^1 e_g^2$ ) |
| (d) all the above electrons paired                |

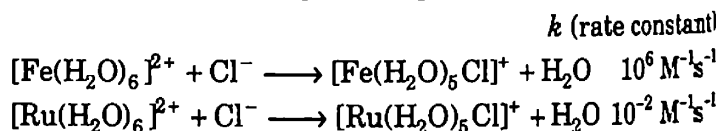
3. Select correct statement.

The CFSE for

- |                                    |                                                     |
|------------------------------------|-----------------------------------------------------|
| (a) $[\text{FeCl}_6]^{3-}$ is zero | (b) $[\text{Fe}(\text{CN})_6]^{3-}$ is $-2\Delta_o$ |
| (c) Both are correct               | (d) None is correct                                 |

### Passage 6

Consider following exchange reactions :



Now answer the following questions

1. Rate constant of the exchange reaction with iron complex is very high. It is attributed to that  $\text{Fe}^{2+}$  complex involving a first-row transition metal is
- |                                          |
|------------------------------------------|
| (a) high-spin $d^6$ and labile           |
| (b) low-spin $d^6$ and kinetically inert |
| (c) paramagnetic and kinetically inert   |
| (d) diamagnetic and kinetically inert    |

2.  $\text{Ru}^{2+}$ , like other second- and third-row transition metal ions
- forms low-spin complexes
  - low-spin  $d^6$  species are kinetically inert
  - both of the above
  - none of the above

### Passage 7

Read the following experiment and answer the questions at the end of it.

"A student in 1895 prepared three coordination compounds containing chromium with the following properties:

| Formula                                       | Colour      | $\text{Cl}^-$ ions in solution per formula units |
|-----------------------------------------------|-------------|--------------------------------------------------|
| (A) $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ | Violet      | 3                                                |
| (B) $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ | Light green | 2                                                |
| (C) $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ | Dark green  | 1                                                |

1. Which complex has maximum molecules of hydration?

- A
- B
- C
- Equally

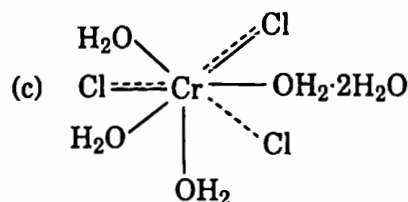
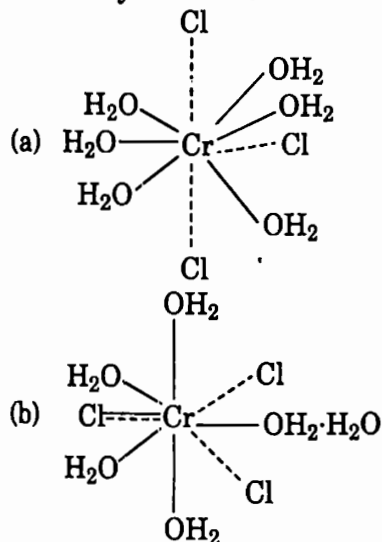
2. IUPAC name of the complex A is

- hexaaquatrachlorochromium (III)
- hexaaquochromium(III)chloride
- pentaaquochlorochromium(III)chloride
- tetraaquodichlorochromium(III)chloride

3. Complexes A, B, C are represented as

- A :  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$   
 B :  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$   
 C :  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$
- A :  $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$   
 B :  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$   
 C :  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
- A :  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$   
 B :  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$   
 C :  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
- none of the above

4. Structural formula of B indicating primary and secondary valencies both is



- (d) None of the above

5. Conducting nature of these complexes in the increasing order is

- $A < B < C$
- $C < A < B$
- $B < A < C$
- $C < B < A$

### Passage 8

Read the following experimental method and answer the questions at the end of it.

A rose-coloured compound has the empirical formula  $\text{CoCl}_3 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$ . Two moles of this compound react with concentrated sulphuric acid to form  $\text{HCl}(g)$  and one mole of a new compound with empirical formula  $\text{Co}_2(\text{SO}_4)_3 \cdot 10\text{NH}_3 \cdot 5\text{H}_2\text{O}$ . When this new compound is dried at room temperature, it loses three moles of water per mol of  $\text{Co}_2(\text{SO}_4)_3 \cdot 10\text{NH}_3 \cdot 5\text{H}_2\text{O}$ .

1. What is the formula of the rose-coloured compound?

- $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
- $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_2$
- $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O}) \cdot \text{Cl}_2]\text{Cl}$
- None of the above

2. What is the structure of the new complex formed?

- $[\text{Co}-(\text{NH}_3)_5-\text{Co}-(\text{NH}_3)_5](\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$
- $[\text{Co}-(\text{NH}_3)_5-\text{Co}-(\text{NH}_3)_5](\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$
- 
- None of the above

### Passage 9

Mr. William isolated two complexes and in Chemical Abstract, he reported

"A metal complex having composition  $\text{Cr}(\text{NH}_3)_4\text{Cl}_2\text{Br}$  has been isolated in two forms (A) and (B). The form (A) reacts with  $\text{AgNO}_3$  to give a white precipitate readily soluble in dilute aqueous ammonia, whereas (B) gives a pale yellow precipitate soluble in concentrated ammonia.

Read the above report from Chemical Abstract and answer the questions at the end of it.

1. Complex A and B are respectively

- $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$ ,  $[\text{Cr}(\text{NH}_3)_4\text{Br}]\text{Cl}_2$
- $[\text{Cr}(\text{NH}_3)_4\text{Br}]\text{Cl}_2$ ,  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$
- $[\text{Cr}(\text{NH}_3)_4\text{ClBr}]\text{Cl}$ ,  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$
- $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$ ,  $[\text{Cr}(\text{NH}_3)_4\text{ClBr}]\text{Cl}$

2. Cr atom is ..... hybridised  
 (a)  $sp^3d^2$  in both complexes  
 (b)  $d^2sp^3$  in both complexes  
 (c)  $sp^3d^2$  in A and  $d^2sp^3$  in B  
 (d)  $d^2sp^3$  in A and  $sp^3d^2$  in B
3. EAN and magnetic moment of Cr in A and B are  
 (a) 33,  $\sqrt{15}$  BM (b) 36,  $\sqrt{15}$  BM  
 (c) 33,  $\sqrt{24}$  BM (d) 36,  $\sqrt{24}$  BM

### Passage 10

Study the following short write up and answer the questions at the end of it.

A, B and C are three complexes of chromium (III) with the empirical formula  $H_{12}O_6Cl_3Cr$ . All the three complexes have water and chloride ions as ligands. Complex A does not react with concentrated  $H_2SO_4$ , whereas complexes B and C lose 6.75% and 13.5% of their original weight respectively, on treatment with concentrated  $H_2SO_4$ .

1. Complex A is  
 (a)  $[Cr(H_2O)_6]Cl_3$   
 (b)  $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$   
 (c)  $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$   
 (d) None of the above
2. Loss in weight on treatment with concentrated  $H_2SO_4$  is due to  
 (a)  $Cl^-$  is lost as HCl  
 (b)  $Cr^{3+}$  is lost as  $Cr_2(SO_4)_3$   
 (c)  $H_2O$  is lost due to absorption  
 (d)  $Cl^-$  is lost as  $Cl_2$
3. Which of the above complexes is maximum hydrated?  
 (a) A (b) B  
 (c) C (d) Equally
4. Select the correct statement(s).  
 (a) Conductance in these complexes is in order  $C < B < A$   
 (b) EAN and nuclear spin of chromium are identical in each complex  
 (c) Non-reactivity of A with conc.  $H_2SO_4$  is due to absence of water molecules outside coordinated sphere  
 (d) All of the above are correct

### Passage 11

Consider following experiments and answer the questions at the end of it.

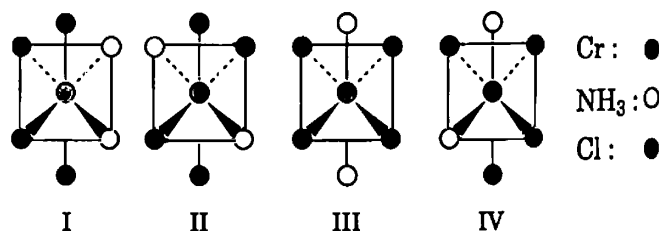
(A) When  $Fe(CN)_2$  solution is treated with KCN solution, species formed, no longer, gives tests of  $Fe^{2+}$  and  $CN^-$ .

(B) When  $K_2SO_4$  solution is treated with  $Al_2(SO_4)_3$  solution, species formed gives tests of  $K^+$ ,  $Al^{3+}$  and  $SO_4^{2-}$ .

1. Species formed in experiment A does not give test of  $Fe^{2+}$  and  $CN^-$ . It is due to formation of  
 (a)  $K_2[Fe(CN)_4]$  (b)  $K_3[Fe(CN)_5]$   
 (c)  $K_3[Fe(CN)_6]$  (d)  $K_4[Fe(CN)_6]$
2. Species formed in experiment (B) is  
 (a) complex (b) double salt  
 (c) liquid crystal (d) None of these
3. EAN of iron formed in (A) is  
 (a) 26 (b) 24  
 (c) 36 (d) 38
4. When the species formed in (A) is treated with  $FeCl_3$ , a blue colour is obtained. It is due to the formation of  
 (a)  $Fe^{II}[Fe^{III}(CN)_6]^-$  (b)  $Fe^{III}[Fe^{II}(CN)_6]^-$   
 (c) both (a) and (b) (d) None of these

### Passage 12

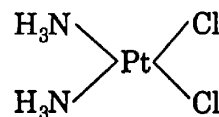
Consider the following isomers of  $[Cr(NH_3)_2Cl_4]^-$  and answer the questions.



1. Out of these isomers  
 (a) I and IV are *trans* and II and III are *cis*  
 (b) I and IV are *cis* and II and III are *trans*  
 (c) I and II are *cis* and III and IV are *trans*  
 (d) I and II are *trans* and III and IV are *cis*
2. Select the correct statement.  
 (a) Pair of I and IV are same and pair of II and III are also same  
 (b) All have chiral centres  
 (c) I and III are enantiomers  
 (d) II and IV are enantiomers

### Passage 13

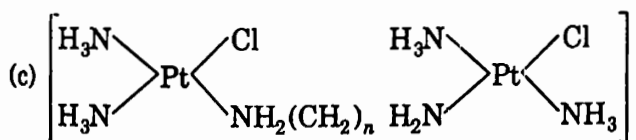
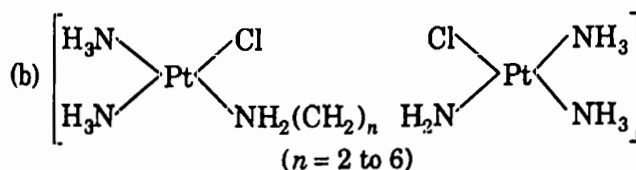
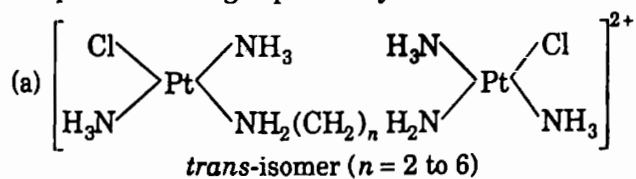
*Cis*-diamminedichloroplatinum (II),  $[Pt(NH_3)_2Cl_2]$ , is



One of the number of platinum coordination compounds is used in the treatment of cancer. Commonly known as **cis-platin**, this compound has the ability to block the uncontrolled division of cancerous cells that results in the growth of tumours. Recent studies show that *cis*-platin can cause serious side effects, including severe kidney damage.

Read the above medical report and answer the following questions.

1. Cis-platin is being replaced by

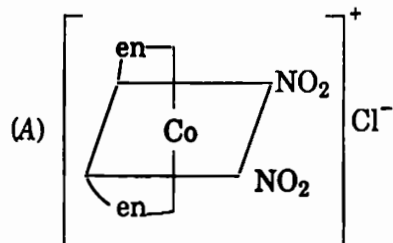


(d) None of the above

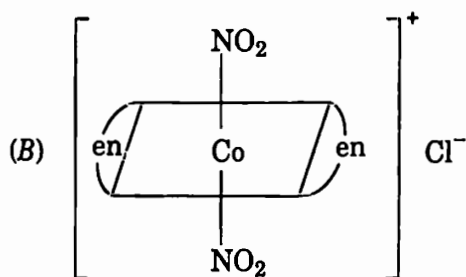
### Passage 14

Following experiment has been given to identify isomer. Read the experiment and answer the questions.

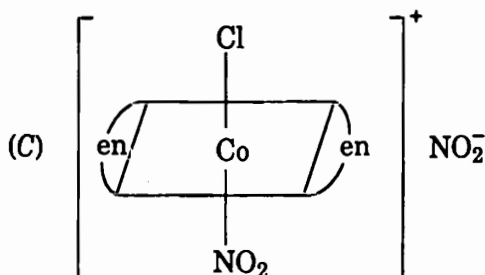
A compound  $\text{Co}(\text{en})_2(\text{NO}_2)_2\text{Cl}$  has been prepared in a number of isomeric forms. One form undergoes no reaction with  $\text{AgNO}_3$  or  $(\text{en})$  and is optically inactive. A second form reacts with  $\text{AgNO}_3$  but not with  $(\text{en})$  and is optically inactive. A third form is optically active and reacts with both  $\text{AgNO}_3$  and  $(\text{en})$ , complexes are:



*cis-bis (ethylenediamine)dinitrocobalt (III) chloride*



*trans-bis (ethylenediamine)dinitrocobalt (III) chloride*



*trans-chloronitrobis(ethylenediamine)cobalt (III) nitrite*

1. First form of the complex is

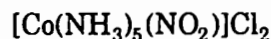
- (a) A (b) B  
(c) C (d) None of these

2. One of the complexes turns KI-starch paper blue in acidic medium. This complex is

- (a) C (b) B  
(c) A (d) all of these

### Passage 15

A research-guide instructed his two students to synthesize complex



They synthesised the complexes with identical molecular formula, molar mass, geometry conductance and spin, but they differed in colour. Based on the above facts answer the following questions.

1. The difference in colour is due to

- (a) optical isomerism  
(b) geometrical isomerism  
(c) linkage isomerism  
(d) nuclear isomerism

2. Which of the ligands can show ambident property?

- (a)  $\text{NO}_2^-$  (b)  $\text{NH}_3$   
(c)  $\text{H}_2\text{O}$  (d)  $\text{CO}_3^{2-}$

3. Complexes synthesized can be

- (a)  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$  (b)  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$   
(c)  $[\text{Co}(\text{NH}_3)_5\text{Cl}_2]\text{NO}_2$  (d) all of these

### Passage 16

Read the following short write-up and answer the questions at the end of it.

One cationic complex has two isomers A and B. Each has one  $\text{Co}^{3+}$ , five  $\text{NH}_3$ , one  $\text{Br}^-$  and one  $\text{SO}_4^{2-}$  stoichiometrically. A gives white ppt with  $\text{BaCl}_2$  while B give yellow ppt with  $\text{AgNO}_3$ .

1. A can be

- (a)  $[\text{Co}(\text{NH}_3)_5]\text{BrSO}_4$   
(b)  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$   
(c)  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$   
(d)  $[\text{Co}(\text{NH}_3)_4\text{SO}_4]\text{Br} \cdot \text{NH}_3$

2. B can be

- (a)  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$   
(b)  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$   
(c)  $[\text{Co}(\text{NH}_3)_3\text{Br}(\text{SO}_4)] \cdot 2\text{NH}_3$   
(d) None of the above

3. Complexes A and B have similarity in the following but not in

- (a) molar conductance (b) van't Hoff factor  
(c) EAN (d) colour



## Assertion & Reason

Codes :

- (a) Both **A** and **R** are true and **R** is the correct explanation of **A**.
- (b) Both **A** and **R** are true but **R** is not the correct explanation of **A**.
- (c) **A** is true but **R** is false.
- (d) **A** is false but **R** is true.

1. **Assertion (A)** : All the iron-carbon bond distances in ferrocene are equal.

**Reason (R)** : The  $\pi$ -electrons in the cyclopentadienyl group of ferrocene are delocalised.

2. **Assertion (A)** : The electronic absorption spectrum of the tetrahedral complex,  $[\text{CoCl}_4]^{2-}$  shows bands which are more intense compared to the absorption bands for the octahedral complex  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ .

**Reason (R)** : The octahedral complexes possess a centre of symmetry.

3. **Assertion (A)** :  $\text{Ni}(\text{CO})_4$  is a diamagnetic complex.

**Reason (R)** : All the electrons in the complex are paired.

4. **Assertion (A)** :  $\text{NO}_2^-$  is an ambident ligand.

**Reason (R)** :  $\text{NO}_2^-$  is a Lewis base.

5. **Assertion (A)** : A stable complex is formed when ethylene diamine (en) is added to  $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$ .

**Reason (R)** : (en) being a strong ligand replaces weak ligand  $\text{H}_2\text{O}$  and thus, chelate is formed.

6. **Assertion (A)** :  $\text{CoCl}_3 \cdot 4\text{NH}_3$  gives two ions when ionised.

**Reason (R)** : Complex is  $[\text{Co}(\text{NH}_3)_4]\text{Cl}_3$ .

7. **Assertion (A)** : Spot of iron-rusting can be removed by addition of oxalic acid.

**Reason (R)** : Water soluble complex is formed with oxalic acid.

## True & False

- Use of *cis*-platin in cancer treatment also causes severe kidney damage.
- Lead poisoning can be removed by use of EDTA.
- Out of  $[\text{Cu}(\text{CN})_4]^{3-}$  and  $[\text{Cd}(\text{CN})_4]^{2-}$ ,  $[\text{Cu}(\text{CN})_4]^{3-}$  is unstable and gives black precipitate of  $\text{CuS}$  on passing  $\text{H}_2\text{S}$  gas.
- $\text{AgBr}$  is soluble in *aq.*  $\text{NH}_3$  as well as in hypo.
- $[\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $[\text{Cu}(\text{CN})_4]^{2-}$  are labile complexes.
- $[\text{Cu}(\text{H}_2\text{O})_4]^{2+} + 4\text{NH}_3 \longrightarrow [\text{Cu}(\text{NH}_3)_4]^{2+} + 4\text{H}_2\text{O}$  is spontaneous in forward side, and  $\Delta G = -ve$
- $[\text{Fe}(\text{CN})_6]^{3-}$  is more stable than  $[\text{Fe}(\text{CN})_6]^{4-}$

- A cyclic multidentate ligand increases the stability of the complex.

- $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  is an inner *d*-complex.

- $\text{H}_2\text{O}$  is a weaker field ligand than  $\text{NH}_3$  and  $\Delta_{\text{oct}}([\text{Cr}(\text{NH}_3)_6]^{3+}) < \Delta_{\text{oct}}([\text{Cr}(\text{H}_2\text{O})_6]^{3+})$

- Orange is the complimentary colour of blue spectral colour.

- $\Delta_t = \frac{4}{9} \Delta_{\text{oct}}$

- The  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals lie between the axes and collectively called  $t_{2g}$  orbitals.

- Geometry of  $[\text{Ni}(\text{CN})_4]^{2-}$  is tetrahedral.

- In the complex  $\text{CoCl}_3 \cdot 5\text{NH}_3$  one  $\text{Cl}^-$  ion satisfies primary and secondary valencies of cobalt(III).

- cis* $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  can have *d* and *l*-optical isomers.

- $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  are linkage isomers.

- CN of Fe in  $[\text{Fe}(\text{en})_3]^{3+}$  is three.

- Ferrocene is stable since  $\pi$ -electrons in cyclopentadienyl ion are delocalised.

- EDTA is hexadentate ligand and is used to remove hardness in water.

## Fill in the Blanks

- Ligands which can be coordinated to a metal or metal ion through either of the sides are called .....
- Vitamin  $\text{B}_{12}$  is a complex of .....
- Haemoglobin is a complex of Fe(II) bound to ..... rings.
- ..... is the number of ligating groups in a multidentate.
- Common name of bicyclopentadienyl iron (II) is .....
- 1 mol of the monohydrate complex  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  on reaction with excess of  $\text{AgNO}_3$  solution gives ..... mol of white precipitate of .....
- $[\text{Pt}(\text{Gly})_2]$  can exist as ..... isomers.
- $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is called ..... orbital complex.
- $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  has O.N. of Fe as ..... and thus magnetic moment of Fe is .....
- The  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals are directed along a set of mutually perpendicular *x*, *y* and *z*-axes and are called ..... orbitals.
- The  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals lie between the axes and collectively called ..... orbitals.
- $\Delta_t = -\frac{4}{9}$  .....

13. Blue-green is the complimentary colour of ..... spectral colour.
14. Strong field ligands, such as  $\text{CN}^-$ , usually produce ..... spin complexes and ..... crystal field splitting.
15. Reaction between  $\text{NH}_3$  and  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  is .....
16.  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $[\text{CuCl}_4]^{2-}$  are called ..... complexes.
17. Stability of a complex with multidentate ligand is increased due to .....
18. Lead poisoning can be decreased by addition of .....
19. Gold and silver are extracted by complex formation with .....
20. Unreacted silver bromide in photographic plate is removed by the addition of .....

## Matrix-Match Type Questions

### I. Only One Correct

1. Match the complex (in List I) with the hybridisation of the central ion (in List II).

| List I                             | List II      |
|------------------------------------|--------------|
| A. $\text{Ni}(\text{CO})_4$        | 1. $sp^3d^2$ |
| B. $[\text{Ni}(\text{CN})_4]^{2-}$ | 2. $sp^3$    |
| C. $[\text{Fe}(\text{CN})_6]^{4-}$ | 3. $d^2sp^3$ |
| D. $[\text{MnF}_6]^{4-}$           | 4. $dsp^2$   |

2. Match the complex (in List I) with the geometry (in List II).

| List I                               | List II                 |
|--------------------------------------|-------------------------|
| A. $[\text{Ni}(\text{CN})_4]^{2-}$   | 1. Tetrahedral          |
| B. $[\text{ZnCl}_4]^{2-}$            | 2. Trigonal bipyramidal |
| C. $[\text{Fe}(\text{CO})_5]$        | 3. Square planar        |
| D. $[\text{Co}(\text{NO}_2)_6]^{4-}$ | 4. Square pyramid       |
|                                      | 5. Octahedral           |

3. Match the complex (in List I) with the equivalent conductance (in List II).

| List I                                                | List II |
|-------------------------------------------------------|---------|
| A. $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$   | 1. 229  |
| B. $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$ | 2. 97   |
| C. $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$   | 3. 404  |
| D. $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$            | 4. 523  |

4. Match the complex (in List I) with the oxidation number of Co (in List II).

| List I                                                 | List II |
|--------------------------------------------------------|---------|
| A. $[\text{Co}(\text{NCS})(\text{NH}_3)_5]\text{SO}_3$ | 1. -1   |
| B. $\text{Na}[\text{Co}(\text{CO})_4]$                 | 2. 0    |
| C. $\text{Na}_4[\text{Co}(\text{S}_2\text{O}_3)_3]$    | 3. +1   |
| D. $\text{Co}_2(\text{CO})_5$                          | 4. +2   |
|                                                        | 5. +3   |

5. Match the complex (in List I) with the type of isomerism (in List II).

| List I                                                        | List II         |
|---------------------------------------------------------------|-----------------|
| A. $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$                    | 1. Optical      |
| B. $\text{cis}[\text{Co}(\text{en})_2\text{Cl}_2]$            | 2. Ionisation   |
| C. $[\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}]\text{SCN}$ | 3. Coordination |
| D. $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$       | 4. Geometrical  |

6. Match complex ion (in List I) with number of unpaired electrons (in List II).

| List I                                      | List II |
|---------------------------------------------|---------|
| A. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ | 1. 0    |
| B. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ | 2. 1    |
| C. $[\text{Fe}(\text{CN})_6]^{4-}$          | 3. 2    |
| D. $[\text{Fe}(\text{CN})_6]^{3-}$          | 4. 3    |
| E. $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$ | 5. 4    |
|                                             | 6. 5    |

### II. One or More Correct

1. Match the complex (in Column I) with its corresponding property (ies) (given in Column II).

| Column I                                            | Column II       |
|-----------------------------------------------------|-----------------|
| A. $[\text{Ni}(\text{DMG})_2]$                      | 1. Chelation    |
| B. $\text{Na}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ | 2. Paramagnetic |
| C. $[\text{Ni}(\text{en})_2]\text{Cl}_2$            | 3. Diamagnetic  |
| D. $\text{Ni}(\text{Co})_4$                         | 4. Conducting   |
|                                                     | 5. H-bonding    |

2. Match the complex (in Column I) with its corresponding property (ies) (in Column II).

| Column I                                                           | Column II                |
|--------------------------------------------------------------------|--------------------------|
| A. $[\text{Cr}(\text{NO}_2)_2(\text{NH}_3)_2\text{Cl}_2]$          | 1. Geometrical isomerism |
| B. $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$                | 2. Ionisation isomerism  |
| C. $[\text{Cr}(\text{en})_3]^{3+}$                                 | 3. Optical isomerism     |
| D. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2][\text{Cu}(\text{CN})_4]$ | 4. Linkage isomerism     |
|                                                                    | 5. Coordinate isomerism  |

## Integer Answer Types

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the ORS have to be darkened. For example, if the correct answers to question number X, Y, Z and W (say) are 6, 0, 9 and 2, respectively

| X | Y | Z | W |
|---|---|---|---|
| ① | ① | ① | ① |
| ② | ② | ② | ② |
| ③ | ③ | ③ | ③ |
| ④ | ④ | ④ | ④ |
| ⑤ | ⑤ | ⑤ | ⑤ |
| ⑥ | ⑥ | ⑥ | ⑥ |
| ⑦ | ⑦ | ⑦ | ⑦ |
| ⑧ | ⑧ | ⑧ | ⑧ |
| ⑨ | ⑨ | ⑨ | ⑨ |

### Set I

1.  $[\text{Co}(\text{NH}_3)_6]^{3+}$  has ..... unpaired electron(s) in  $t_{2g}$  orbitals.
2. There are ..... electron in  $e_g$  orbitals is  $[\text{CoF}_6]^{3-}$
3. There are ..... electron in  $t_{2g}$  orbitals in  $[\text{CoF}_6]^{3-}$
4. In the high spin complexes of  $\text{Cr}^{3+}$  number of unpaired electron in  $t_{2g}$  orbitals is .....
5. Total number of ions due to ionisation of the complex  $\text{CoCl}_3 \cdot 6\text{H}_2\text{O}$  is .....
6. Total number of orbitals used in hybridisation of octahedral complex  $[\text{Fe}(\text{CN})_6]^{3-}$  is .....

7. Square-planar  $[\text{Ni}(\text{CN})_4]^{2-}$  uses .....  $d$ -orbital(s) in hybridisation.

8. CFSE of high-spin  $d^5$ - $\text{Mn}^{2+}$  complex is .....

### Set II

This section contains 10 questions.

1. Ionisable chloride ions in  $\text{CoCl}_5 \cdot 4\text{NH}_3$  are .....
2. Magnetic moment of a complex is 4.9 B.M. Thus, unpaired electron(s) may be .....
3. Nickel dimethylglyoximate is stable due to chelation. Chelate ring(s) is/are .....
4. Ethylenediamine displaces  $\text{H}_2\text{O}$  in the complex  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  in three steps  

$$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + 3\text{en} \longrightarrow [\text{Fe}(\text{en})_3]^{3+} + 6\text{H}_2\text{O}$$
Stepwise formation constants are

$$\log k_1 = 4.34$$

$$\log k_2 = 3.31$$

$$\log k_3 = 2.05$$

Overall formation constant is  $A \times 10^B$   
 A is .....

5. B in question (4) is .....
6. Ambidentate ligands out of  
 $\text{Py}$ ,  $\text{en}$ ,  $\text{CNS}$ ,  $\text{CN}$ ,  $\text{CNO}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{NO}_2$ , are
7. EDTA is a multidentate ligand. Its denticity (multicity) is .....
8.  $\text{CrCl}_3 \cdot \text{H}_2\text{O}$  loses 13.5% water on treatment with conc.  $\text{H}_2\text{SO}_4$ . Number of water molecules lost is .....
9. Number of aromatic rings in ferrocene is .....
10. Effective atomic number of Ni in  $\text{Ni}(\text{CO})_x$  is 36.  
 Thus,  $x = \dots\dots\dots$

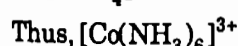
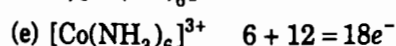
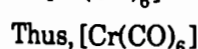
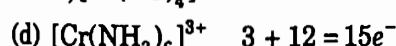
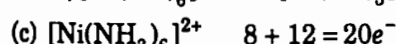
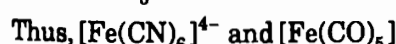
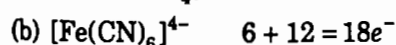
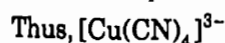
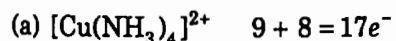
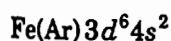
# Answers & Solutions

## Master Exercises

### Exercise 1

#### Short Answer Type Questions

1. To obey the rule of 18 (EAN), the sum of the number of electrons in the metal valence shell  $[(n-1)dsp]$  and those donated by the ligands should be 18, filling the low-energy metal orbitals.



2.  $[\text{Cu}(\text{NH}_3)_2\text{Cl}_2] < \text{KNO}_3 < \text{Na}_2[\text{PtCl}_6] < [\text{Co}(\text{NH}_3)_6]\text{Cl}_3$   
 neutral      two ions      three ions      four ions

Larger the number of ions, greater the electrical conductivity.

3.  $[\text{Fe}(\text{CN})_6]^{3-}$  has the strongest field ligands of the three complexes; thus, its energy levels are split by the greatest amount. The frequency of the light absorbed should be greatest, and  $\lambda_{\text{max}}$  should be the shortest for this ion.

$[\text{Fe}(\text{CN})_6]^{4-}$  : red colour — absorb blue-violet light

$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  : pale violet — absorb red light

$[\text{FeF}_6]^{3-}$  : colourless — absorb light in visible spectrum

4.  $[\text{Co}(\text{NH}_3)_6]^{2+}$  is paramagnetic due to presence of one electron unpaired in presence of strong field ligand (low-spin complex).

5. Monodentate

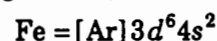
N-atom is bonded to metal ion

| 6.  | Ligand                                                                      | Unpaired electron (b) | CFSE (c)                 |
|-----|-----------------------------------------------------------------------------|-----------------------|--------------------------|
| I.  | $[\text{Fe}(\text{CN})_6]^{3-}$ ( $d^5$ ) strong (low spin complex)         | 1                     | $-\frac{10}{5} \Delta_o$ |
| II. | $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ( $d^5$ ) weak (high spin complex) | 5                     | zero                     |

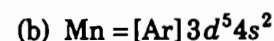
(a)  $[\text{Fe}(\text{CN})_6]^{3-}$  has fewer unpaired electron

7. Yellow

8. (a) The overall charge is  $-1$ , which is equal to the charge on the  $\text{C}_5\text{H}_5^-$  group. Thus, the Fe atom must have no charge. Thus,



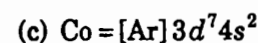
(6 electrons from  $\text{C}_5\text{H}_5^-$ ) + (8 electrons from Fe) + (4 electrons from 2 CO groups) =  $18e^-$



Valence electrons in  $\text{Mn}^- = 8$

Electrons donated of 5CO = 10

Thus,  $8 + 10 = 18e^-$



Electrons of  $\text{Co}^+ = 8$

Electrons donated by  $\text{C}_5\text{H}_5^- = 6$

Electrons donated by two  $\text{C}_2\text{H}_4 = 4$

Thus,  $8 + 6 + 4 = 18e^-$

9. In  $[\text{NiCl}_4]^{2-}$   $\text{Cl}^-$  is a weak ligand thus electrons are unpaired in  $\text{Ni}^{2+}$  making it paramagnetic  $sp^3$ -tetrahedral structure

When strong ligand  $\text{CN}^-$  is added, substitution takes place and electrons are paired in  $[\text{Ni}(\text{CN})_4]^{2-}$   $dsp^2$  — square planar.

10. Blue green

11.  $\text{Fe}^{2+}$  —  $[\text{Ar}] 3d^6$  high spin — four unpaired electrons  
low spin — none unpaired electrons

### Analytical Questions

1. (i) 35 (ii) 33 (iii) 33

| 2.   | (a) | (b) | (c) | (d) | (e) |
|------|-----|-----|-----|-----|-----|
| C.N. | 6   | 6   | 4   | 6   | 2   |
| O.N. | 2   | 3   | 2   | 3   | 1   |

| 3.  | Ligands                    | C.N. | O.N. |
|-----|----------------------------|------|------|
| (a) | $\text{NH}_3, \text{NO}_2$ | 6    | +3   |
| (b) | CN                         | 6    | +2   |
| (c) | $\text{NH}_3, \text{Cl}$   | 6    | +3   |
| (d) | $\text{NH}_3$              | 4    | +2   |
| (e) | CN                         | 2    | +1   |
| (f) | en                         | 6    | +3   |

4. Only two-third of the chlorine is precipitated indicating that two chlorine atoms are outside coordinate sphere. Thus, complex can be  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ . It also ionises as  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + 2\text{Cl}^-$

5.  $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$ ; C.N. of Pt = 6

$[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$ ; C.N. of Pt = 6

6. Moles of the complex =  $\frac{23.25}{233.5} = 0.1$

Moles of AgCl ppt =  $\frac{14.35}{143.5} = 0.1$

Thus, 1 mole of the complex gives 1 mole of AgCl indicating only one chlorine is outside coordinate sphere. Thus, complex is  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ .

7.  $n = 5$  8. See text

9. (a) Pentamminecarbonatechromium (III) chloride  
(b) Pentamminenitritocobalt (III) chloride  
(c) Potassium hexacyanochromate (III)  
(d) Hexammine cobalt (III) chloride

10. (a)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  (b)  $\text{Li}[\text{AlH}_4]$

11. See text 12. See text 13. See text 14. See text

15. (a) and (b) are identical

(a) and (d) are geometrical isomers

(c) is distinct

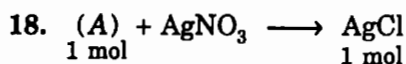
16. (a) I, II, IV — Chiral

II — Achiral

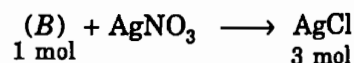
(b) Refer text

(c) I, IV are enantiomers

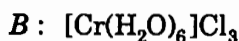
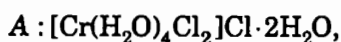
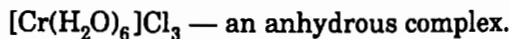
17. Refer text



Thus, (A) has only one ionisable Cl atom. Thus, A is



Thus, (B) has three ionisable Cl-atoms. Thus, B is



A will change to  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$  on heating being hydrated complex. B has no effect of heating, all  $\text{H}_2\text{O}$  molecules being ligands. A will ionise as  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$  and  $\text{Cl}^-$

B will ionise as  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  and  $3\text{Cl}^-$  hence conductance of B is greater than that of A.

19. A :  $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{H}_2\text{O})]\text{SO}_4$  B :  $[\text{Co}(\text{NH}_3)_4(\text{SO}_4)(\text{H}_2\text{O})]\text{Cl}$   
C :  $[\text{Co}(\text{NH}_3)_4(\text{SO}_4)\text{Cl}] \cdot \text{H}_2\text{O}$

A and B are ionisation isomers, C is hydrate isomer each of A and B.

(You can also make geometrical isomers of each)

20. A does not lose water with conc.  $\text{H}_2\text{SO}_4$  indicating that  $\text{H}_2\text{O}$  are in coordinate sphere.

Thus, A is  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$

Molar mass of the complex =  $52 + 108 + 106.5$   
 $= 266.5 \text{ g mol}^{-1}$

After loss with conc.  $\text{H}_2\text{SO}_4$  in (B) =  $\frac{266.5 \times 93.25}{100}$   
 $= 249.18$

Net loss =  $266.5 - 249.18$

$= 17.32 \text{ g} = 1 \text{ mol H}_2\text{O}$

Thus, one water molecule is lost per molecule of the complex. Thus, complex (B) is



After loss with conc.  $\text{H}_2\text{SO}_4$ , molar mass of (C) is

$= \frac{266.5 \times 86.5}{100}$

$= 230.52 \text{ g mol}^{-1}$

Net loss =  $35.98 \text{ g}$

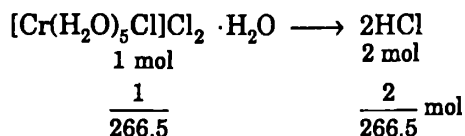
Number of water molecules lost =  $\frac{35.98}{18} = 2$ . Thus, two

$\text{H}_2\text{O}$  molecules are as hydrate molecules.

Thus, (C) is  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$

21. While passing through the cation exchanger there is formation of HCl. Molar mass of the complex  $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_2 = 52 + 108 + 106.5$

$= 266.5 \text{ g mol}^{-1}$



$$[\text{HCl}] = 7.5 \times 10^{-3} \text{ M}$$

$$= 7.50 \times 10^{-3} \times 36.5 \text{ gL}^{-1}$$

$$= 0.24 \text{ gL}^{-1}$$

$$\Delta E = \frac{hc}{\lambda}$$

$$= \frac{6.62 \times 10^{-34} \times 3 \times 10^6}{544 \times 10^{-9}}$$

$$= 3.65 \times 10^{-19} \text{ J mol}^{-1}$$

$$= 3.65 \times 10^{-19} \times 6.02 \times 10^{23} \text{ J mol}^{-1}$$

$$= 219.79 \text{ kJ mol}^{-1}$$

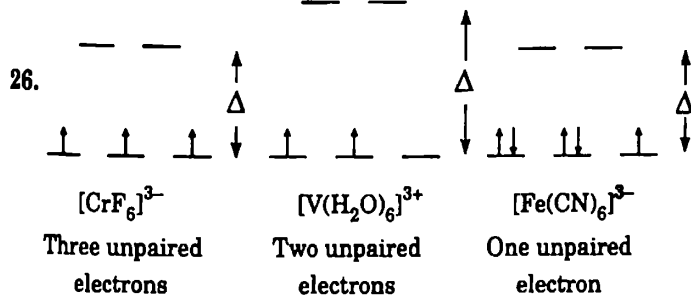
22.

23. (a) 3 unpaired electrons; (b) paramagnetic;

(c)  $[\text{FeCl}_4]^-$  has the greater number of unpaired electrons than  $[\text{Mn}(\text{CN})_6]^{3-}$ . $\text{Cl}^-$  — a weak ligand $\text{CN}^-$  — a strong ligand24.  $[\text{Co}(\text{en})_3]^{3+}$  --- yellow $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  --- blueSince (en) produces greater  $d$ -level splitting than does  $\text{H}_2\text{O}$ .

25. (a) inner, paramagnetic (b) outer, paramagnetic

(c) inner, diamagnetic (d) inner, paramagnetic

27.  $[\text{Fe}(\text{CN})_6]^{3-}$  has  $d^2sp^3$  (inner  $d$ -complex) hybridisation with one electron unpaired while  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  has  $sp^3d^2$  (outer  $d$ -complex) hybridisation with five unpaired electrons

$$\text{magnetic moment} = \sqrt{N(N+2)} \text{ BM}$$

where,  $N$  is the number of unpaired electrons.

28. (b) 29. Only (c) is correct 30. (I) (c) (II) (d)

31. (c) They differ in number of unpaired electrons.

32. Refer text

33. A :  $[\text{Cr}(\text{NH}_3)_4\text{ClBr}]\text{Cl}$ B :  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$ Cr is  $d^2sp^3$ -hybridisedunpaired electrons  $N = 3$ 

$$\text{magnetic moment} = \sqrt{N(N+2)} \text{ BM} = \sqrt{15} \text{ BM}$$

34. Also text for structures.

| Hybridisation                                         | Unpaired electron | Magnetic moment       |
|-------------------------------------------------------|-------------------|-----------------------|
| $[\text{NiCl}_4]^{2-} sp^3$ , tetrahedral             | 2                 | $\sqrt{8} \text{ BM}$ |
| $[\text{Ni}(\text{CN})_4]^{2-} dsp^2$ , square planar | 0                 | 0                     |

35. EDTA can form complex with lead present in the body. Calcium salt is preferred otherwise calcium of the body will also be removed as calcium-EDTA complex (that is harmful).

36. (a)  $\text{Al}^{3+}$  forms a hydroxo compound such as  $[\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4]^-$  but not an ammine complex;(b) Solubility product ( $K_{sp}$ ) for  $\text{ZnS}$  is much smaller than for  $\text{ZnCO}_3$ , and a saturated solution of  $\text{ZnS}$  does not produce a large enough  $[\text{Zn}^{2+}]$  for the complex ion to form;(c)  $[\text{Co}^{3+}]$  is kept sufficiently low in a solution of the stable complex ion,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , that it is unable to oxidise water.

37. (a) One can determine conductance;

(b) One can determine freezing point;

(c) One can detect  $\text{Al}^{3+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ .

## NCERT Problems

1. (a) oxalate (b) six (c) oxalate

2. (a) +3 (b) +2 (c) +3 (d) +3 (e) +3

3. (a)  $[\text{Zn}(\text{OH})_4]^{2-}$  (b)  $[\text{Co}(\text{NH}_3)_6](\text{SO}_4)_3$  (c)  $\text{K}_2[\text{PdCl}_4]$ (d)  $\text{K}_3[\text{Cr}(\text{OX})_3]$  (e)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ (f)  $[\text{Pt}(\text{NH}_3)_6]^{4+}$  (g)  $\text{K}_2[\text{Ni}(\text{CN})_4]$  (h)  $[\text{CuBe}_4]^{2-}$ (i)  $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$  (j)  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$ 

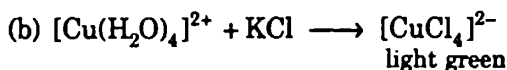
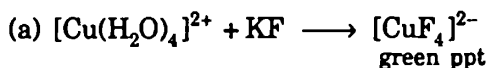
4. Refer text.

5. Refer text.

6. Refer text.

7. Refer text.

8. Refer text.

9. (a)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (b)  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (c)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ 10. Aqueous  $\text{CuSO}_4$  is  $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ 

11. Refer text.

12. Refer text.

13. (a)  $\text{CH}_3\text{—Li}$  (b)  $\text{Si}(\text{CH}_3)_4$  (c)  $\text{Bi}(\text{CH}_3)_3$ (d)  $\text{As}(\text{CH}_3)_3$  (e)  $\text{Al}(\text{CH}_3)_3$  (f)  $\text{B}(\text{CH}_3)_3$ 

14. Refer text.

## Exercise 2

## Only One Option Correct

1. (b) 2. (c)

3. (d) Complex is  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 

$$[[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + 2\text{Cl}^-] y = 3 \text{ ions per mol}$$

$$i = \text{van't Hoff factor} = 1 + (y - 1)x = 3$$

$$\pi = MSTi = 1 \times 0.0821 \times 300 \times 3$$

$$= 73.89 \text{ atm.}$$

Thus, (d)

4. (c) 5. (a) 6. (a) 7. (c) 8. (b)

9. (c)  $\text{Zn}^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Zn}(\text{NH}_3)_4]^{2+}$ 

$$K_f = \frac{[\text{Zn}(\text{NH}_3)_4]^{2+}}{[\text{Zn}^{2+}][\text{NH}_3]^4}$$

$$= 3 \times 10^9$$

$$\therefore \frac{[\text{Zn}(\text{NH}_3)_4]^{2+}}{[\text{Zn}^{2+}]} = [\text{NH}_3]^4 \times 3 \times 10^9$$

$$= 10^4 \times 3 \times 10^9$$

$$= 3 \times 10^{13}$$

$$\therefore \frac{[\text{Zn}^{2+}]}{[\text{Zn}(\text{NH}_3)_4]^{2+}} = 3.3 \times 10^{-14}$$

Hence, (c)

10. (c)

11. (c) 100 mL of 0.024 M = 0.0024 mol of the complex

complex is  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  and thus, one  $\text{Cl}^-$  is formed per mol of the complex which gives 1 mole of  $\text{AgCl}$ .

Hence,  $\text{AgCl}$  formed = 0.0024 mol

Hence, (c)

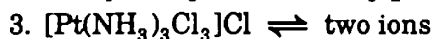
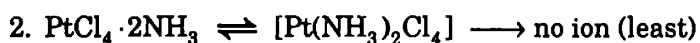
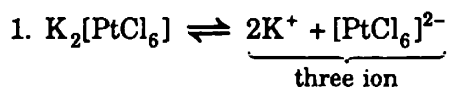
12. (a) 13. (b) 14. (b) 15. (a) 16. (d)

17. (b) 18. (a) 19. (b) 20. (d) 21. (c)

22. (a) 23. (b) 24. (a) 25. (b) 26. (b)

27. (d) 28. (a) 29. (a) 30. (a)

31. (a) Greater the number of ions, greater the conductance.

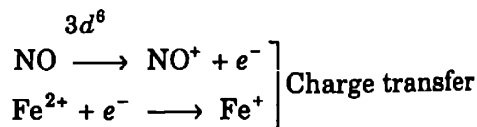
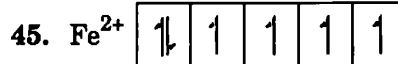


Hence, (a)

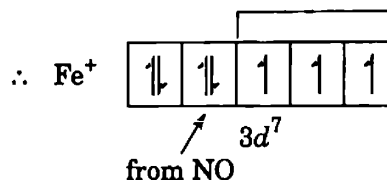
32. (d) 33. (d) 34. (a) 35. (b) 36. (d)

37. (a) 38. (b) 39. (a) 40. (c) 41. (d)

42. (a) 43. (c) 44. (b)



three unpaired electrons



Thus, (a), (b), (c) are true.

Hence, (d)

46. (b) 47. (c) 48. (a) 49. (d) 50. (a)

51. (a) 52. (b) 53. (a) 54. (b) 55. (a)

56. (a) 57. (b) 58. (d) 59. (c) 60. (b)

61. (d) 62. (c) 63. (d) 64. (c)

## One or More Than One Options Correct

1. (a), (b), (c), (d) 2. (b), (c) 3. (a), (c) 4. (c)

5. (a), (b), (c) 6. (c) 7. (c) 8. (c)

9. (a), (b), (c), (d) 10. (a), (b), (d) 11. (b) 12. (b)

13. (d) 14. (a) 15. (b)

## Passage Comprehension Questions

## Passage 1

1. (a) 2. (c) 3. (a)

## Passage 2

1. (a) 2. (b) 3. (b) 4. (c)

## Passage 3

1. (d) 2. (b) 3. (c)

## Passage 4

1. (b) 2. (b) 3. (d)

## Passage 5

1. (b) 2. (a) 3. (c)

## Passage 6

1. (a) 2. (c)

## Passage 7

1. (c) 2. (b) 3. (a) 4. (b) 5. (d)

## Passage 8

1. (b) 2. (d)

### Passage 9

1. (c)      2. (b)      3. (a)

### Passage 10

- 1. (a)      2. (c)      3. (a)      4. (d)**

### Passage 11

- 1. (d)      2. (b)      3. (c)      4. (c)**

### Passage 12

- 1. (b)      2. (a)**

### Passage 13

1. (a)

### Passage 14

- 1. (c)      2. (a)**

### Passage 15

- 1. (c)      2. (a)      3. (a), (b)**

### Passage 16

- 1. (c)      2. (a)      3. (d)**

### Assertion & Reason

1. (b)    2. (b)    3. (a)    4. (b)    5. (a)    6. (c)  
7. (a)

## True & False

- 1. T    2. T    3. F    4. F    5. T    6. T    7. T**

- 8. T    9. F    10. F    11. T    12. F    13. T    14. F**

- 15. T    16. T    17. F    18. F    19. T    20. T**

## Fill in the Blanks

1. ambidentate      2. cobalt    3. porphyrin    4. Denticity

5. ferrocene      7. two, AgCl      8. *cis*-, and *trans*

8. outer      9.  $+1, \sqrt{15}$  B.M.      10.  $e_g$       11.  $t_{2g}$

- 12.  $\Delta_{\text{act}}$     13. red    14. low, large    15. spontaneous**

- 16. labile      17. chelation      18. EDTA      19.  $\text{CN}^-$**

- 20. hypo ( $\text{Na}_2\text{S}_2\text{O}_3$ )**

### Matrix-Match Type Questions

### I. Only One Correct

1. (A)—(2); (B)—(4); (C)—(3); (D)—(1);

2. (A)—(3); (B)—(1); (C)—(2); (D)—(5);  
3. (A)—(3); (B)—(1); (C)—(2); (D)—(4);  
4. (A)—(5); (B)—(1); (C)—(4); (D)—(2);  
5. (A)—(4); (B)—(1); (C)—(2); (D)—(3);  
6. (A)—(5); (B)—(6); (C)—(1); (D)—(2);  
(E)—(3)

## II. One or More Correct

1. (A)—(1,3,5); (B)—(1,2,4); (C)—(1,3,4); (D)—(3);  
2. (A)—(1,4); (B)—(1,2); (C)—(3); (D)—(1,4,5);

## Integer Answer Types

## Set I

| Questions → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|-------------|---|---|---|---|---|---|---|---|
| Answers →   | 0 | 2 | 2 | 3 | 4 | 6 | 1 | 0 |
|             | ① | ① | ① | ① | ① | ① | ① | ① |
|             | ② | ② | ② | ② | ② | ② | ② | ② |
|             | ③ | ③ | ③ | ③ | ③ | ③ | ③ | ③ |
|             | ④ | ④ | ④ | ④ | ④ | ④ | ④ | ④ |
|             | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ | ⑤ |
|             | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ | ⑥ |
|             | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ | ⑦ |
|             | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ | ⑧ |
|             | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ | ⑨ |

## Set II

[illegible]



12-13

# 19

## Salt Analysis

"Salt-analysis is the "Magic-show" of chemists playing with colours."

### Quick Points

- **Common-ion Effect** Ionisation of weak electrolyte or sparingly soluble salt is decreased in presence of common ion. It is called **common-ion effect**.

- Ionisation of weak acid (say  $\text{CH}_3\text{COOH}$ ) is decreased in presence of  $\text{CH}_3\text{COONa}$  (with  $\text{CH}_3\text{COO}^-$  as common ion)
- Ionisation of weak base (say  $\text{NH}_4\text{OH}$ ) is decreased in presence of  $\text{NH}_4\text{Cl}$  (with  $\text{NH}_4^+$  as common ion)
- Solubility of sparingly soluble salt (say  $\text{AgCl}$ ) is decreased in presence of  $\text{AgNO}_3$  ( $\text{Ag}^+$  as common ion) or  $\text{KCl}$  ( $\text{Cl}^-$  as common ion)

- Solubility product of solute  $\text{A}_x\text{B}_y$  is represented as

$$K_{sp} = [\text{A}^{y+}]^x [\text{B}^{x-}]^y = x^x y^y s^{x+y}$$

where,  $s$  is the solubility of solute  $\text{A}_x\text{B}_y$  (in  $\text{mol L}^{-1}$ )

|                                |                   |
|--------------------------------|-------------------|
| For $\text{AgCl}$ ,            | $K_{sp} = s^2$    |
| $\text{Mg}(\text{OH})_2$ ,     | $K_{sp} = 4s^3$   |
| $\text{Al}(\text{OH})_3$ ,     | $K_{sp} = 27s^4$  |
| $\text{Fe}_2(\text{SO}_4)_3$ , | $K_{sp} = 108s^5$ |

- Any solute  $\text{AB}$  is precipitated if

$$[\text{A}^+][\text{B}^-] > K_{sp}$$

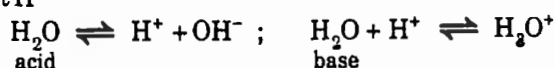
- Salts have been divided into groups based on common-ion effect and solubility product.

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pH} + \text{pOH} = 14 = \text{p}K_w$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14} \text{ at } 298 \text{ K}$$

- Species is said to be amphoteric if it acts as an acid as well as a base. It is amphiprotic if can donate  $\text{H}^+$  ion as well as can accept  $\text{H}^+$



### Learning Framework of the Chapter ...

- Physical Examination
- Analysis of Acid (Anion) Radicals
- Analysis of Basic (Cation) Radicals
- Dry Tests
- One Reagent for Testing Different Ions

## Physical Examination

### Solubility Rules for Common Compounds

The following solubility rules are not comprehensive, but they cover most of the compounds you encountered in general chemistry. Compounds that dissolve in water to the extent of approximately 0.02 mol per litre (0.02 M) are usually classified as “soluble” compounds, while those that are less soluble are classified as “insoluble” compounds. None of the gaseous or solid substances are infinitely soluble in water.

1. All common inorganic acids are soluble in water. Low molecular weight organic acids are soluble.
2. All common compounds of the group IA metal (Na, K, etc.) and the ammonium ion,  $\text{NH}_4^+$ , are soluble in water.
3. All common nitrates  $\text{NO}_3^-$ , acetates,  $\text{CH}_3\text{COO}^-$ , and perchlorates,  $\text{ClO}_4^-$ , are soluble in water.
4. (a) All common chlorides,  $\text{Cl}^-$ , are soluble in water except  $\text{AgCl}$ ,  $\text{Hg}_2\text{Cl}_2$ , and  $\text{PbCl}_2$ .  
(b) The common bromides,  $\text{Br}^-$ , and iodides,  $\text{I}^-$ , show approximately the same solubility behaviour as chlorides, but there are some exceptions. As the halide ions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ), increase in size, the solubilities of their slightly soluble compounds decrease. Although  $\text{HgCl}_2$  is readily soluble in water,  $\text{HgBr}_2$  is only slightly soluble and  $\text{HgI}_2$  is even less soluble.  
(c) The solubilities of the pseudo-halide ions,  $\text{CN}^-$  (cyanide) and  $\text{SCN}^-$  (thiocyanate), are quite similar to those of the corresponding iodides. Additionally, both  $\text{CN}^-$  and  $\text{SCN}^-$  show strong tendencies to form soluble complex compounds.
5. All common sulphates,  $\text{SO}_4^{2-}$ , are soluble in water except  $\text{PbSO}_4$ ,  $\text{Hg}_2\text{SO}_4$ , and  $\text{BaSO}_4$ ;  $\text{CaSO}_4$ , and  $\text{Ag}_2\text{SO}_4$  are sparingly soluble.
6. All common metal hydroxides are insoluble in water except those of the group IA metals and the lower members of the group IIA metals, beginning with  $\text{Ca(OH)}_2$ .
7. All common carbonates,  $\text{CO}_3^{2-}$ , phosphates,  $\text{PO}_4^{3-}$ , and arsenates,  $\text{AsO}_4^{3-}$ , are insoluble in water except those of the group IA metals and  $\text{NH}_4^+$ .  $\text{MgCO}_3$  is fairly soluble.
8. All common sulphides,  $\text{S}^{2-}$  are insoluble in water except those of the group IA and group IIA metals and the ammonium ion. Solubility and colour of different salts are given in Table 19.1

Table 19.1 Solubility and Colour of Different Salts

| Salt/Complex          | Formula                                | Colour                                           | $\left( \begin{array}{c} \text{Soluble} \\ \text{Insoluble} \end{array} \right)$ |
|-----------------------|----------------------------------------|--------------------------------------------------|----------------------------------------------------------------------------------|
|                       |                                        |                                                  | In water                                                                         |
| Ammonium carbonates   | $(\text{NH}_4)_2\text{CO}_3$           | white                                            | soluble                                                                          |
| Ammonium chloride     | $\text{NH}_4\text{Cl}$                 | white                                            | soluble                                                                          |
| Ammonium nitrate      | $\text{NH}_4\text{NO}_3$               | white                                            | soluble                                                                          |
| Ammonium phosphate    | $(\text{NH}_4)_3\text{PO}_4$           | white                                            | soluble                                                                          |
| Ammonium oxalate      | $(\text{NH}_4)_2\text{C}_2\text{O}_4$  | white                                            | soluble                                                                          |
| Ammonium sulphate     | $(\text{NH}_4)_2\text{SO}_4$           | white                                            | soluble                                                                          |
| Ammonium dichromate   | $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ | orange (due to $\text{Cr}_2\text{O}_7^{2-}$ ion) | soluble                                                                          |
| Ammonium molybdate    | $(\text{NH}_4)_2\text{MoO}_4$          | white                                            | soluble in presence of $\text{NH}_4\text{OH}$                                    |
| Arsenic(III) sulphide | $\text{As}_2\text{S}_3$                | yellow                                           | insoluble                                                                        |
| Arsenic(V) sulphide   | $\text{As}_2\text{S}_5$                | yellow                                           | insoluble                                                                        |
| Arsenic(III) iodide   | $\text{AsI}_3$                         | red                                              | insoluble                                                                        |
| Antimony sulphide     | $\text{Sb}_2\text{S}_3$                | orange                                           | insoluble                                                                        |
| Antimonyl chloride    | $\text{SbOCl}$                         | orange                                           | insoluble                                                                        |
| Antimony iodide       | $\text{SbI}_3$                         | red-yellow                                       | insoluble                                                                        |
| Bismuth sulphide      | $\text{Bi}_2\text{S}_3$                | black                                            | insoluble                                                                        |
| Bismuth iodide        | $\text{BiI}_3$                         | black                                            | insoluble                                                                        |
| Bismuth hydroxide     | $\text{Bi(OH)}_3$                      | white                                            | insoluble                                                                        |
| Bismuthyl chloride    | $\text{BiOCl}$                         | white                                            | insoluble                                                                        |
| Bismuth(V) oxide      | $\text{Bi}_2\text{O}_5$                | brown                                            | insoluble                                                                        |
| Bismuthyl iodide      | $\text{BiOI}$                          | red-orange                                       | insoluble                                                                        |
| Barium chloride       | $\text{BaCl}_2$                        | white                                            | soluble                                                                          |

| Salt/Complex                          | Formula                                             | Colour                                          | (Soluble<br>Insoluble)                                                                                  |
|---------------------------------------|-----------------------------------------------------|-------------------------------------------------|---------------------------------------------------------------------------------------------------------|
|                                       |                                                     |                                                 | In water                                                                                                |
| Barium nitrate                        | Ba(NO <sub>3</sub> ) <sub>2</sub>                   | white                                           | soluble                                                                                                 |
| Barium sulphate                       | BaSO <sub>4</sub>                                   | white                                           | insoluble                                                                                               |
| Barium chromate                       | BaCrO <sub>4</sub>                                  | yellow (due to CrO <sub>4</sub> <sup>2-</sup> ) | insoluble (also in CH <sub>3</sub> COOH) but<br>soluble in dil. HCl                                     |
| Chromium(III) oxide                   | Cr <sub>2</sub> O <sub>3</sub>                      | green                                           | insoluble                                                                                               |
| Chromium sulphate                     | Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>     | green                                           | partially soluble                                                                                       |
| Chromium chloride                     | CrCl <sub>3</sub>                                   | green                                           | soluble                                                                                                 |
| Chromium chloride (mineral)           | CrCl <sub>3</sub> · 6H <sub>2</sub> O               | violet                                          | soluble                                                                                                 |
| Chromyl chloride                      | CrO <sub>2</sub> Cl <sub>2</sub>                    | orange red gas                                  | soluble giving H <sub>2</sub> CrO <sub>4</sub>                                                          |
| Chromium hydroxide                    | Cr(OH) <sub>3</sub>                                 | dark green                                      | insoluble                                                                                               |
| Chromate ion                          | CrO <sub>4</sub> <sup>2-</sup>                      | yellow                                          | soluble (salts of alkali and<br>ammonium ion)                                                           |
| Copper(I) sulphide (cupric sulphide)  | Cu <sub>2</sub> S                                   | black                                           | insoluble                                                                                               |
| Copper(II) sulphide (cupric sulphide) | CuS                                                 | black                                           | insoluble                                                                                               |
| Hydrated copper (II) sulphate         | CuSO <sub>4</sub> · 5H <sub>2</sub> O               | blue                                            | soluble                                                                                                 |
| Anhydrous copper(II) sulphate         | CuSO <sub>4</sub>                                   | white                                           | soluble (colour changes to blue)                                                                        |
| Copper(II) hydroxide                  | Cu(OH) <sub>2</sub>                                 | sky blue                                        | insoluble                                                                                               |
| Copper(II) chloride (cupric chloride) | CuCl <sub>2</sub>                                   | bluish green                                    | soluble                                                                                                 |
| Copper(I) oxide (cuprous oxide)       | Cu <sub>2</sub> O                                   | red                                             | insoluble                                                                                               |
| Cuprous iodide                        | Cu <sub>2</sub> I <sub>2</sub>                      | white                                           | insoluble                                                                                               |
| Cuprous thiosulphate                  | Cu <sub>2</sub> S <sub>2</sub> O <sub>3</sub>       | white                                           | soluble                                                                                                 |
| Tetrammine copper(II) sulphate        | [Cu(NH <sub>3</sub> ) <sub>4</sub> ]SO <sub>4</sub> | deep blue                                       | soluble (insoluble in ethanol)                                                                          |
| Cupric ferrocyanide                   | Cu <sub>2</sub> [Fe(CN) <sub>6</sub> ]              | brown                                           | insoluble                                                                                               |
| Cupric oxide, (copper(II) oxide)      | CuO                                                 | black                                           | insoluble                                                                                               |
| Copper(II) cyanide                    | Cu(CN) <sub>2</sub>                                 | yellow                                          | insoluble                                                                                               |
| Copper(I) cyanide                     | CuCN                                                | white                                           | insoluble                                                                                               |
| Copper(II) thiocyanate                | Cu(SCN) <sub>2</sub>                                | black                                           | insoluble                                                                                               |
| Copper(I) thiocyanate                 | CuSCN                                               | white                                           | insoluble                                                                                               |
| Cobalt sulphide                       | CoS                                                 | black                                           | insoluble                                                                                               |
| Potassium cobalti nitrite             | K <sub>3</sub> [Co(NO <sub>2</sub> ) <sub>6</sub> ] | yellowish orange                                | insoluble                                                                                               |
| Cobalt(II) chloride dihydrate         | CoCl <sub>2</sub> · 2H <sub>2</sub> O               | brown                                           | soluble                                                                                                 |
| Cobalt(II) chloride tetrahydrate      | CoCl <sub>2</sub> · 4H <sub>2</sub> O               | brown                                           | soluble                                                                                                 |
| Cobalt(II) chloride hexahydrate       | CoCl <sub>2</sub> · 6H <sub>2</sub> O               | red                                             | soluble                                                                                                 |
| Cobalt(II) cyanide                    | Co(CN) <sub>2</sub>                                 | buff-coloured                                   | insoluble                                                                                               |
| Cadmium oxide                         | CdO                                                 | brown                                           | insoluble                                                                                               |
| Cadmium sulphide                      | CdS                                                 | yellow                                          | insoluble                                                                                               |
| Cadmium carbonate                     | CdCO <sub>3</sub>                                   | white                                           | partly soluble                                                                                          |
| Cadmium hydroxide                     | Cd(OH) <sub>2</sub>                                 | white                                           | insoluble                                                                                               |
| Dichromate ion                        | Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>        | orange                                          | soluble                                                                                                 |
| Zinc sulphide                         | ZnS                                                 | white                                           | insoluble                                                                                               |
| Zinc hydroxide                        | Zn(OH) <sub>2</sub>                                 | white                                           | insoluble, soluble in acid as Zn <sup>2+</sup> ,<br>soluble in alkali as ZnO <sub>2</sub> <sup>2-</sup> |
| Zinc oxide                            | ZnO                                                 | white                                           | (-do-)                                                                                                  |
| Zinc carbonate                        | ZnCO <sub>3</sub>                                   | white                                           | insoluble                                                                                               |
| Lead sulphite                         | PbSO <sub>3</sub>                                   | white                                           | insoluble                                                                                               |
| Lead sulphate                         | PbSO <sub>4</sub>                                   | white                                           | insoluble                                                                                               |
| Lead chloride                         | PbCl <sub>2</sub>                                   | white                                           | soluble in hot water                                                                                    |

| Salt/Complex                                         | Formula                                                              | Colour          | (Soluble)<br>(Insoluble)                                                                                                         |
|------------------------------------------------------|----------------------------------------------------------------------|-----------------|----------------------------------------------------------------------------------------------------------------------------------|
|                                                      |                                                                      |                 | In water                                                                                                                         |
| Lead bromide                                         | PbBr <sub>2</sub>                                                    | white           | soluble in hot water                                                                                                             |
| Lead oxide (litharge)                                | PbO                                                                  | orange-red      | insoluble                                                                                                                        |
| Lead double oxide                                    | 2PbO · PbO <sub>2</sub> (Pb <sub>3</sub> O <sub>4</sub> )            | red             | insoluble                                                                                                                        |
| Lead dioxide                                         | PbO <sub>2</sub>                                                     | blackish brown  | insoluble                                                                                                                        |
| Lead carbonate                                       | PbCO <sub>3</sub>                                                    | white           | insoluble                                                                                                                        |
| Lead chromate (basic)                                | PbO · PbCrO <sub>4</sub>                                             | red             | insoluble                                                                                                                        |
| Lead chromate                                        | PbCrO <sub>4</sub>                                                   | yellow          | insoluble (soluble in HNO <sub>3</sub> as PbCr <sub>2</sub> O <sub>7</sub> and in NaOH as [Pb(OH) <sub>4</sub> ] <sup>2-</sup> ) |
| Lead iodide                                          | PbI <sub>2</sub>                                                     | yellow          | insoluble                                                                                                                        |
| Lead sulphide                                        | PbS                                                                  | black           | insoluble                                                                                                                        |
| Lead hydroxide                                       | Pb(OH) <sub>2</sub>                                                  | white           | insoluble (soluble in NaOH as [Pb(OH) <sub>4</sub> ] <sup>2-</sup> )                                                             |
| Lead cyanide                                         | Pb(CN) <sub>2</sub>                                                  | white           | insoluble                                                                                                                        |
| Lead carbonate (basic)                               | PbO · PbCO <sub>3</sub>                                              | white           | insoluble                                                                                                                        |
| Lead phosphate                                       | Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>                      | white           | insoluble                                                                                                                        |
| Manganese dioxide                                    | MnO <sub>2</sub>                                                     | brownish-red    | insoluble                                                                                                                        |
| Manganese sulphide                                   | MnS                                                                  | buff coloured   | insoluble                                                                                                                        |
| Manganese chloride                                   | MnCl <sub>2</sub>                                                    | light pink      | soluble                                                                                                                          |
| Manganese hydroxide                                  | Mn(OH) <sub>2</sub>                                                  | light pink      | insoluble                                                                                                                        |
| Permanganate (potassium)                             | KMnO <sub>4</sub>                                                    | violet (purple) | soluble                                                                                                                          |
| Manganate (potassium)                                | K <sub>2</sub> MnO <sub>4</sub>                                      | green           | soluble                                                                                                                          |
| Manganese oxide                                      | MnO                                                                  | green           | insoluble                                                                                                                        |
| Manganese carbonate                                  | MnCO <sub>3</sub>                                                    | brown           | insoluble                                                                                                                        |
| Calcium chloride                                     | CaCl <sub>2</sub>                                                    | white           | soluble                                                                                                                          |
| Calcium carbonate                                    | CaCO <sub>3</sub>                                                    | white           | insoluble                                                                                                                        |
| Calcium oxalate                                      | CaC <sub>2</sub> O <sub>4</sub>                                      | white           | insoluble                                                                                                                        |
| Calcium nitrate                                      | Ca(NO <sub>3</sub> ) <sub>2</sub>                                    | white           | soluble                                                                                                                          |
| Calcium bicarbonate                                  | Ca(HCO <sub>3</sub> ) <sub>2</sub>                                   | white           | soluble                                                                                                                          |
| Calcium sulphate                                     | CaSO <sub>4</sub>                                                    | white           | insoluble                                                                                                                        |
| Magnesium chloride                                   | MgCl <sub>2</sub>                                                    | white           | soluble                                                                                                                          |
| Magnesium ammonium phosphate                         | Mg(NH <sub>4</sub> )PO <sub>4</sub>                                  | white           | insoluble                                                                                                                        |
| Iron(III) oxide                                      | Fe <sub>2</sub> O <sub>3</sub>                                       | red             | insoluble                                                                                                                        |
| Iron(II) carbonate                                   | FeCO <sub>3</sub>                                                    | green           | soluble                                                                                                                          |
| Iron(II) chloride                                    | FeCl <sub>2</sub>                                                    | green           | soluble                                                                                                                          |
| Iron(II) sulphide                                    | FeS                                                                  | black           | insoluble                                                                                                                        |
| I                                                    | FeS <sub>2</sub>                                                     | yellow          | insoluble                                                                                                                        |
| Iron(II) phosphate                                   | Fe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>                      | brown           | insoluble                                                                                                                        |
| Iron(III) hexacyanoferrate(II) (Prussian blue) ion   | Fe <sup>III</sup> [Fe <sup>II</sup> (CN) <sub>6</sub> ] <sup>-</sup> | blue            | soluble, Fe <sub>4</sub> [Fe(CN) <sub>6</sub> ] <sub>3</sub><br>insoluble                                                        |
| Iron(II) hexacyanoferrate(III) ion (Turnbull's blue) | Fe <sup>II</sup> [Fe(CN) <sub>6</sub> ] <sup>-</sup>                 | blue            | soluble                                                                                                                          |
| Complex of S <sup>2-</sup> with sodium nitroprusside | Na <sub>2</sub> [Fe(CN) <sub>5</sub> NOS]                            | purple          | soluble                                                                                                                          |
| Magnetite                                            | Fe <sub>3</sub> O <sub>4</sub>                                       | red             | insoluble                                                                                                                        |
|                                                      | [Fe(CNS)] <sup>2+</sup>                                              | blood red       | soluble                                                                                                                          |
| Iron(III) carbonate                                  | Fe <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>                      | red             | insoluble                                                                                                                        |
| Iron(III) fluoride                                   | FeF <sub>3</sub>                                                     | white           | insoluble                                                                                                                        |
| Iron(II) fluoride                                    | FeF <sub>2</sub>                                                     | green           | insoluble                                                                                                                        |

| Salt/Complex                               | Formula                                                                                                                                            | Colour          | (Soluble)<br>insoluble                                                             |
|--------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------|-----------------|------------------------------------------------------------------------------------|
|                                            |                                                                                                                                                    |                 | in water                                                                           |
| Iron(III) oxalate                          | $\text{Fe}_2(\text{C}_2\text{O}_4)_3$                                                                                                              | blackish-red    | insoluble                                                                          |
| Iron(III) hydroxide                        | $\text{Fe}(\text{OH})_3$                                                                                                                           | reddish-brown   | insoluble                                                                          |
| Mercury(II) sulphide                       | $\text{HgS}$                                                                                                                                       | black           | insoluble                                                                          |
| Mercury(I) oxide                           | $\text{Hg}_2\text{O}$                                                                                                                              | black           | insoluble                                                                          |
| Mercury(II) chloride (corrosive sublimate) | $\text{HgCl}_2$                                                                                                                                    | white           | soluble                                                                            |
| Mercury(I) chloride (calomel)              | $\text{Hg}_2\text{Cl}_2$                                                                                                                           | white           | insoluble                                                                          |
| Mercury(II) bromide                        | $\text{HgBr}_2$                                                                                                                                    | white           | insoluble                                                                          |
|                                            | $\text{HgNH}_2\text{Cl} \cdot \text{HgO}$                                                                                                          | black           | insoluble                                                                          |
| Mercury(II) oxide                          | $\text{HgO}$                                                                                                                                       | yellow          | insoluble                                                                          |
| Mercury(II) iodide                         | $\text{HgI}_2$                                                                                                                                     | reddish orange  | insoluble                                                                          |
| Iodide of Millon's base                    | $\text{Hg} \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{O} \\ \diagdown \quad \diagup \\ \text{Hg} \quad \text{I} \end{array}$ | brown           | insoluble                                                                          |
| Mercury(I) chromate                        | $\text{Hg}_2\text{CrO}_4$                                                                                                                          | red             | insoluble                                                                          |
| Mercury(I) carbonate                       | $\text{Hg}_2\text{CO}_3$                                                                                                                           | yellowish white | insoluble                                                                          |
| Mercury(I) hydrogen phosphate              | $\text{HgHPO}_4$                                                                                                                                   | white           | insoluble                                                                          |
| Mercury(II) cyanide                        | $\text{Hg}(\text{CN})_2$                                                                                                                           | white           | soluble                                                                            |
| Nickel sulphide                            | $\text{NiS}$                                                                                                                                       | black           | insoluble                                                                          |
| Nickel chloride                            | $\text{NiCl}_2$                                                                                                                                    | green           | soluble                                                                            |
| Nickel hydroxide                           | $\text{Ni}(\text{OH})_2$                                                                                                                           | green           | insoluble                                                                          |
| Nickel(III) oxide                          | $\text{Ni}_2\text{O}_3$                                                                                                                            | black           | insoluble                                                                          |
| Silver chloride                            | $\text{AgCl}$                                                                                                                                      | white           | insoluble (soluble in aq. $\text{NH}_3$ as $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ ) |
| Silver bromide                             | $\text{AgBr}$                                                                                                                                      | yellow          | insoluble                                                                          |
| Silver iodide                              | $\text{AgI}$                                                                                                                                       | yellow          | insoluble                                                                          |
| Silver sulphide                            | $\text{Ag}_2\text{S}$                                                                                                                              | black           | insoluble                                                                          |
| Silver oxide                               | $\text{Ag}_2\text{O}$                                                                                                                              | black/brown     | insoluble                                                                          |
| Silver thiosulphate                        | $\text{Ag}_2\text{S}_2\text{O}_3$                                                                                                                  | white           | insoluble                                                                          |
| Silver nitrate                             | $\text{AgNO}_3$                                                                                                                                    | white crystals  | soluble                                                                            |
| Silver phosphate                           | $\text{Ag}_3\text{PO}_4$                                                                                                                           | yellow          | insoluble                                                                          |
| Silver carbonate                           | $\text{Ag}_2\text{CO}_3$                                                                                                                           | yellowish white | insoluble                                                                          |
| Silver arsenate                            | $\text{Ag}_3\text{AsO}_4$                                                                                                                          | red             | insoluble                                                                          |
| Silver chromate                            | $\text{Ag}_2\text{CrO}_4$                                                                                                                          | red             | insoluble                                                                          |
| Silver sulphite                            | $\text{Ag}_2\text{SO}_3$                                                                                                                           | white           | insoluble                                                                          |
| Silver arsenite                            | $\text{Ag}_3\text{AsO}_3$                                                                                                                          | yellow          | insoluble                                                                          |
| Silver arsenate                            | $\text{Ag}_3\text{AsO}_4$                                                                                                                          | brownish red    | insoluble                                                                          |
| Tin(IV) sulphide                           | $\text{SnS}_2$                                                                                                                                     | yellow          | insoluble                                                                          |
| Tin(II) chloride                           | $\text{SnCl}_2$                                                                                                                                    | white           | soluble                                                                            |
| Tin(II) sulphide                           | $\text{SnS}$                                                                                                                                       | brown           | insoluble                                                                          |
| Tin(II) iodide                             | $\text{SnI}_2$                                                                                                                                     | red             | insoluble                                                                          |
| Strontium carbonate                        | $\text{SrCO}_3$                                                                                                                                    | white           | insoluble                                                                          |
| Strontium sulphate                         | $\text{SrSO}_4$                                                                                                                                    | white           | (insoluble in dilute mineral acid)                                                 |
| Strontium sulphite                         | $\text{SrSO}_3$                                                                                                                                    | white           | insoluble                                                                          |
| Strontium oxalate                          | $\text{SrC}_2\text{O}_4$                                                                                                                           | white           | insoluble in $\text{CH}_3\text{COOH}$ but soluble in mineral acids                 |

## A Convenient Classification of Bases

- Strong soluble bases**  
Bases that are soluble in water and are completely, or nearly completely, ionised (dissociated) in dilute aqueous solutions. The only *common* strong soluble bases are the hydroxides of the group IA metals and the hydroxides of the lower members of the group IIA metals.  $\text{Ca(OH)}_2$  and  $\text{Sr(OH)}_2$  have limited solubilities but are classified as strong soluble bases. Most metal hydroxides are "insoluble" in water.
- Weak soluble bases**  
Bases that are soluble in water but which ionise only slightly in dilute aqueous solutions. Aqueous ammonia and its low molecular weight organic derivatives, the amines, are common weak soluble bases.
- Insoluble bases**  
Bases that are very slightly soluble in water. As a matter of common usage, very slightly soluble bases are called "insoluble" bases. With the exception of those listed as strong soluble bases, all common low oxidation state metal hydroxide are "insoluble".
- Amphoteric hydroxides (Bases)**  
Insoluble bases that react with both acids and strong soluble bases to complex ions of the general formula  $[\text{M(OH)}_n]^{x-}$  where " $n$ " varies from 3 to 6 and " $x$ " is either 1 or 2 and metalloids which form amphoteric hydroxides are listed together with the formula for the amphoteric hydroxides and the complex ions formed in an excess of strong soluble bases.

| Metal ion or metalloid | Insoluble amphoteric hydroxide | Complex ion formed in an excess of a strong soluble base |
|------------------------|--------------------------------|----------------------------------------------------------|
| $\text{Be}^{2+}$       | $\text{Be(OH)}_2$              | $[\text{Be(OH)}_4]^{2-}$                                 |
| $\text{Al}^{3+}$       | $\text{Al(OH)}_3$              | $[\text{Al(OH)}_4]^-$                                    |
| $\text{Cr}^{3+}$       | $\text{Cr(OH)}_3$              | $[\text{Cr(OH)}_4]^-$                                    |
| $\text{Zn}^{2+}$       | $\text{Zn(OH)}_2$              | $[\text{Zn(OH)}_4]^{2-}$                                 |
| $\text{Sn}^{2+}$       | $\text{Sn(OH)}_2$              | $[\text{Sn(OH)}_3]^-$                                    |
| $\text{Sn}^{4+}$       | $\text{Sn(OH)}_4$              | $[\text{Sn(OH)}_6]^{2-}$                                 |
| $\text{Pb}^{2+}$       | $\text{Pb(OH)}_2$              | $[\text{Pb(OH)}_4]^{2-}$                                 |
| $\text{As}^{3+}$       | $\text{As(OH)}_3$              | $[\text{As(OH)}_4]^-$                                    |
| $\text{Sb}^{3+}$       | $\text{Sb(OH)}_3$              | $[\text{Sb(OH)}_4]^-$                                    |
| $\text{Si}^{4+}$       | $\text{Si(OH)}_4$              | $\text{SiO}_4^{4-}$ and $\text{SiO}_3^{2-}$              |
| $\text{Co}^{2+}$       | $\text{Co(OH)}_2$              | $[\text{Co(OH)}_4]^{2-}$                                 |
| $\text{Cu}^{2+}$       | $\text{Cu(OH)}_2$              | $[\text{Cu(OH)}_4]^{2-}$                                 |

## Metal Hydroxides that are Soluble in Excess Aqueous Ammonia

Some metal hydroxides dissolve in an excess of aqueous ammonia to form soluble complex compounds. The common examples are listed in the Table 19.2.

**Table 19.2 Common Metal Ions that Forms Ammine Complexes with an Excess of Aqueous Ammonia**

| Metal ions           | Insoluble hydroxides formed by limiting amount aq. $\text{NH}_3$ | Complex ion formed by excess aq. $\text{NH}_3$ |
|----------------------|------------------------------------------------------------------|------------------------------------------------|
| $\text{Co}^{2+}(* )$ | $\text{Co(OH)}_2$                                                | $[\text{Co(NH}_3)_6]^{2+}$                     |
| $\text{Co}^{3+}$     | $\text{Co(OH)}_3$                                                | $[\text{Co(NH}_3)_6]^{3+}$                     |
| $\text{Ni}^{2+}$     | $\text{Ni(OH)}_2$                                                | $[\text{Ni(NH}_3)_6]^{2+}$                     |
| $\text{Cu}^{+}(**)$  | $\text{CuOH} \longrightarrow \frac{1}{2} \text{Cu}_2\text{O}$    | $[\text{Cu(NH}_3)_2]^+$                        |
| $\text{Cu}^{2+}(* )$ | $\text{Cu(OH)}_2$                                                | $[\text{Cu(NH}_3)_4]^{2+}$                     |
| $\text{Ag}^{+}(**)$  | $\text{AgOH} \longrightarrow \frac{1}{2} \text{Ag}_2\text{O}$    | $[\text{Ag(NH}_3)_2]^+$                        |
| $\text{Zn}^{2+}$     | $\text{Zn(OH)}_2$                                                | $[\text{Zn(NH}_3)_4]^{2+}$                     |
| $\text{Cd}^{2+}$     | $\text{Cd(OH)}_2$                                                | $[\text{Cd(NH}_3)_4]^{2+}$                     |
| $\text{Hg}^{2+}$     | $\text{Hg(OH)}_2$                                                | $[\text{Hg(NH}_3)_4]^{2+}$                     |

\* $\text{Co(OH)}_2$  and  $\text{Cu(OH)}_2$  are only slightly amphoteric, i.e., a very large excess of strong soluble base is required to dissolve small amounts of these insoluble hydroxides.

\*\* $\text{CuOH}$  and  $\text{AgOH}$  are unstable and decompose to the corresponding oxides.

The common ions of Rh, Ir, Pd, Pt, and Au show similar behaviour, but since these ions are seldom encountered in elementary courses, they are not included here. Note that these metals and those in the table are all members of the Co, Ni, Cu, and Zn families of the Periodic Table.

## Colour Change on Heating

Certain oxides change colour on heating and this fact can be used to identify salt.

| Oxides                                   | Colour  |                 |
|------------------------------------------|---------|-----------------|
|                                          | In cold | on heating      |
| $\text{ZnO}$                             | white   | yellow          |
| $\text{SnO}_2$ , $\text{Bi}_2\text{O}_3$ | yellow  | yellowish brown |
| $\text{Fe}_2\text{O}_3$                  | brown   | black/red       |
| $\text{PbO}$                             | yellow  |                 |

| Observation                                            | Inference              |
|--------------------------------------------------------|------------------------|
| (i) Sublimate formed with smell of $\text{NH}_3$       | $\text{NH}_4^+$ salts  |
| (ii) Sublimation formed without smell of $\text{NH}_3$ | $\text{Hg}^{2+}$ salts |
| (iii) Brown fumes                                      | Some nitrates          |

## Analysis of Acid (Anion) Radicals

Salt or mixture is treated with dil.  $\text{H}_2\text{SO}_4$  and also with conc.  $\text{H}_2\text{SO}_4$  separately and by observing the types of gases evolved, confirmatory tests of anions are performed.

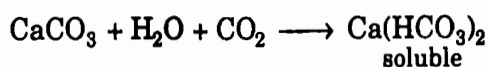
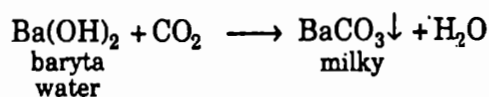
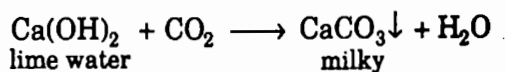
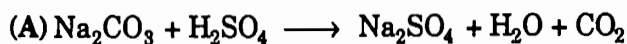
### Observation with Dilute $\text{H}_2\text{SO}_4$

| S. no. | Observation                                                            | Acid radical                                  | Confirmatory test*                                                                                                                                       |
|--------|------------------------------------------------------------------------|-----------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1.     | Brisk effervescence with evolution of colourless and odourless gas     | $\text{CO}_3^{2-}$<br>(carbonate)             | Gas turns lime water (or baryta water) milky but milkyness disappears on passing gas in excess (A)*                                                      |
| 2.     | Brown fumes                                                            | $\text{NO}_2^-$<br>(nitrite)                  | Add KI and starch solution—blue colour (B)*                                                                                                              |
| 3.     | Smell of rotten eggs ( $\text{H}_2\text{S}$ smell) on heating          | $\text{S}^{2-}$<br>(sulphide)                 | Gas turns lead acetate paper black (C)<br>Sodium carbonate extract (SE)† + sodium nitroprusside solution — purple colour (D)                             |
| 4.     | Colourless gas with pungent smell of burning sulphur                   | $\text{SO}_3^{2-}$<br>(sulphite)              | Gas turns acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution green [(E), different from $\text{CO}_3^{2-}$ ] since gas also turns lime water milky (F) |
| 5.     | Solution gives smell of vinegar                                        | $\text{CH}_3\text{COO}^-$<br>(acetate)        | Aqueous solution + neutral $\text{FeCl}_3 \rightarrow$ blood red colour (G) changing to brownish red ppt on boiling                                      |
| 6.     | White or yellowish white turbidity on warming due to colloidal sulphur | $\text{S}_2\text{O}_3^{2-}$<br>(thiosulphate) | Aqueous solution + $\text{AgNO}_3 \rightarrow$ white ppt changing to black (H) on warming                                                                |

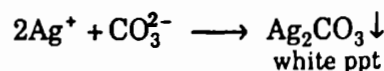
\* (A), (B) ..... indicates reaction number given separately.

† SE is prepared by boiling mixture and  $\text{Na}_2\text{CO}_3$  (1 : 3) in  $\text{H}_2\text{O}$  and filtering. Filtrate has soluble sodium salt of anions.

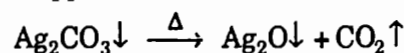
### Carbonate



- Soluble carbonate gives white precipitate of silver carbonate with silver nitrate

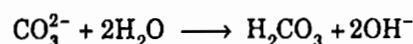


The precipitate is soluble in nitric acid and in ammonia. The precipitate becomes yellow or brown upon addition of excess reagent owing to the forming of silver oxide; the same happens if the mixture is boiled:



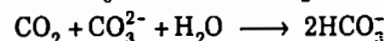
### DEEP Focus

- Aqueous carbonate solution is alkaline due to hydrolysis (with  $\text{H}_2\text{O}$ )

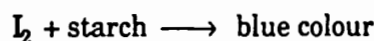
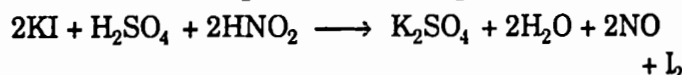
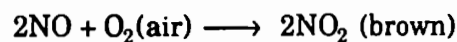
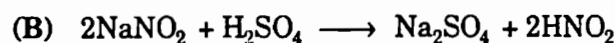


Alkaline solution turns pink when a drop of phenolphthalein is added to it.

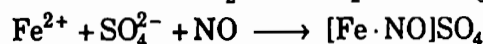
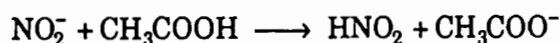
If  $\text{CO}_2$  (liberated from the reaction of given carbonate with dilute  $\text{H}_2\text{SO}_4$ ) is passed into above pink-coloured solution, then it is decolourised by  $\text{HCO}_3^-$  formed with  $\text{CO}_2$ .



### Nitrite

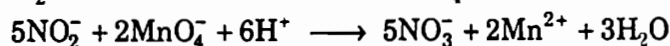


When the nitrite solution is added carefully to a saturated solution of iron(II) sulphate acidified with acetic acid or with dilute sulphuric acid, a brown ring, due to the compound  $[\text{Fe} \cdot \text{NO}]\text{SO}_4$ , is formed at the junction of two liquids.

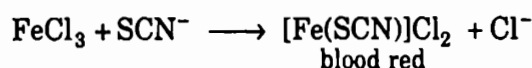
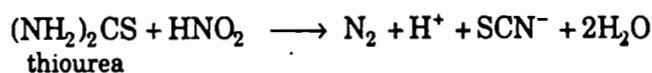


Iodides, bromides, coloured ions, and anions that give coloured compounds with iron(II) ions must be absent.

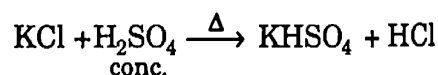
$\text{NO}_2^-$  solution also decolourises  $\text{MnO}_4^-/\text{H}^+$

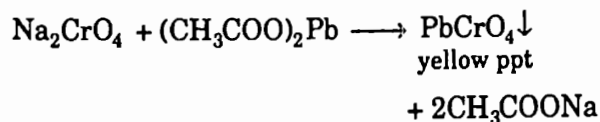
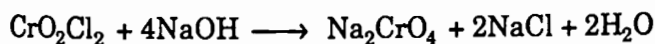
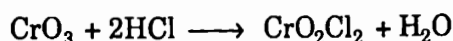
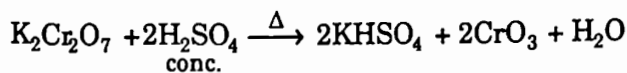
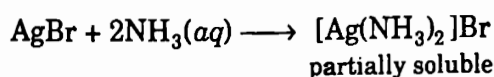
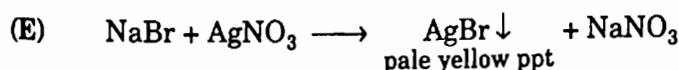
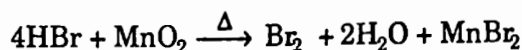
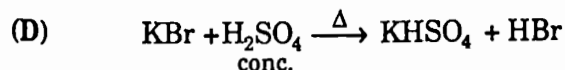


$\text{NO}_2^-$  in  $\text{CH}_3\text{COOH}$  solution on treatment with thiourea forms  $\text{SCN}^-$  which gives red colour with  $\text{FeCl}_3$  and  $\text{HCl}$ .

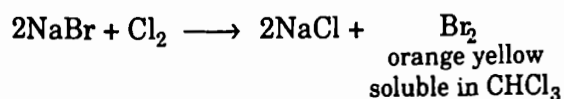




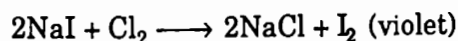
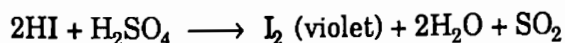
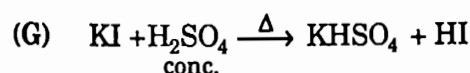


**Bromide****(F) Layer Test**

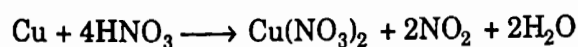
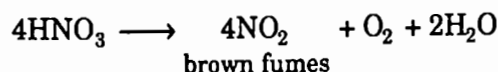
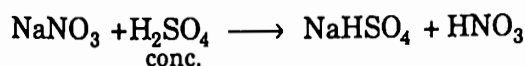
SE +  $\text{Cl}_2$  water +  $\text{CHCl}_3 \xrightarrow{\text{shake}}$  yellowish orange colour in  $\text{CHCl}_3$  layer ( $\text{CS}_2$  or  $\text{CCl}_4$  can be taken instead of  $\text{CHCl}_3$ )



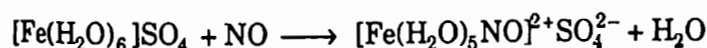
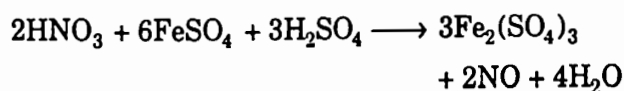
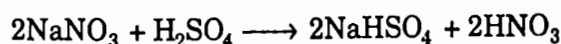
In case of  $\text{I}^-$ , violet colour of  $\text{I}_2$  in  $\text{CHCl}_3$  layer (H)

**Iodide**

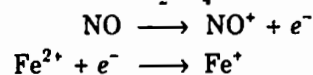
(H) **Layer Test** See (F) above.

**Nitrate**

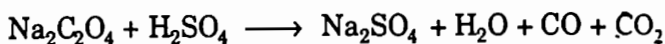
(I) **Ring Test** To water extract (all  $\text{NO}_3^-$  are water soluble) add freshly prepared  $\text{FeSO}_4$  solution and then conc.  $\text{H}_2\text{SO}_4$  carefully by the side of the test-tube. A dark brown ring of  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^+\text{SO}_4^{2-}$  at the interface between the two liquids is formed.

**DEEP Focus**

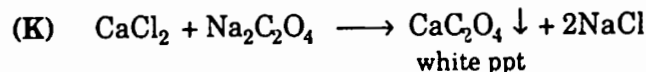
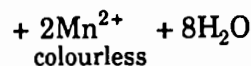
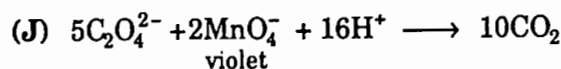
The colour is due to charge transfer. This complex formally contains Fe (+I) and  $\text{NO}^+$  since Fe(II) gains one electron from NO which changes to  $\text{NO}^+$ . Its magnetic moment is 3.87 B.M. confirming the presence of three unpaired electrons. Nitrites give the brown colour before  $\text{H}_2\text{SO}_4$  is added.



The ring test is unreliable in the presence of bromide, iodide, nitrite, chlorate and chromate, hence must be removed before ring-test of  $\text{NO}_3^-$  is performed.

**Oxalate**

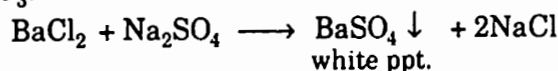
CO burns with blue flame and  $\text{CO}_2$  turns lime water milky.



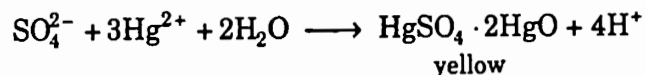
$\text{CaC}_2\text{O}_4$  decolourises acidified  $\text{KMnO}_4$ .

**Specific Tests in Solution****(A) Sulphate**

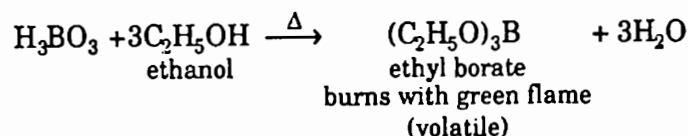
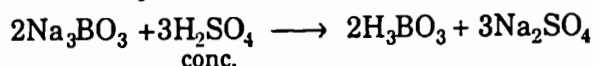
To SE add dil. HCl (to decompose  $\text{CO}_3^{2-}$  until reaction ceases). Add  $\text{BaCl}_2$  solution. White ppt insoluble in conc.  $\text{HNO}_3$ .



$\text{Hg}(\text{NO}_3)_2$  gives yellow precipitate of basic mercury (II) sulphate

**(B) Borate**

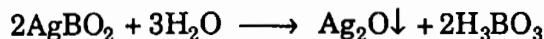
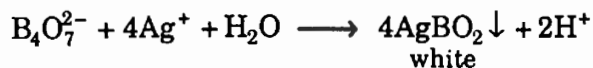
Ignite the mixture containing borate, conc.  $\text{H}_2\text{SO}_4$  and ethanol in a china-dish with a burning splinter—green edged flame of ethyl borate.



In presence of  $\text{Cu}^{2+}$ , perform this test in a test-tube since  $\text{Cu}^{2+}$  salts are not volatile.

$\text{AgNO}_3$  gives white precipitate of silver metaborate  $\text{AgBO}_2$  from fairly concentrated borax solution, soluble in

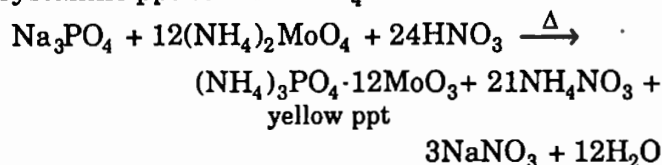
dilute aq.  $\text{NH}_3$  and in  $\text{CH}_3\text{COOH}$ . On boiling the precipitate with  $\text{H}_2\text{O}$ , a brown precipitate of  $\text{Ag}_2\text{O}$  is obtained due to hydrolysis.



Barium salts also give white precipitate of  $\text{Ba}(\text{BO}_2)_2$  barium metaborate.

### (C) Phosphate

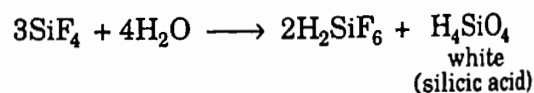
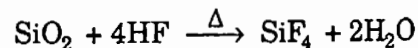
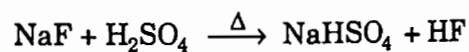
SE +  $\text{HNO}_3$  + ammonium molybdate solution. Heat; yellow crystalline ppt confirms  $\text{PO}_4^{3-}$ .



**Arsenate ion also gives this test. Hence, presence of phosphate should also be checked after group II.**

### (D) Fluoride

Sand + salt ( $\text{F}^-$ ) + conc.  $\text{H}_2\text{SO}_4$ ; heat and bring a water-wetted rod in contact with vapours at the mouth of the test-tube. A white deposit on the rod shows the presence of  $\text{F}^-$ .



## Target Practice 1

1. It is experimental facts that all common inorganic acids dissolve in water. What are the ions formed if acid is  $\text{HCl}$ ?

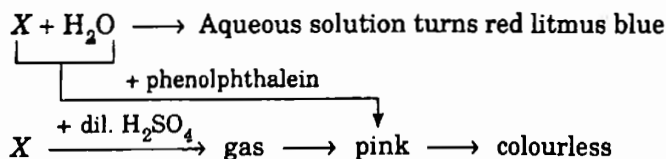
2. Specify the colour and soluble/insoluble character in water of the following

|       | Salt                        | Colour | Soluble/Insoluble |
|-------|-----------------------------|--------|-------------------|
| (i)   | $\text{CuCl}$               | .....  | .....             |
| (ii)  | $\text{CuCl}_2$             | .....  | .....             |
| (iii) | $\text{KI}$                 | .....  | .....             |
| (iv)  | $\text{I}_2$                | .....  | .....             |
| (v)   | $\text{I}_2$ in $\text{KI}$ | .....  | .....             |
| (vi)  | $\text{KNO}_3$              | .....  | .....             |

3. Specify the cases in which soluble nature of the salt changes?

- (a)  $\text{KCN}$  is added to  $\text{AgCl}$  (insoluble) .....
- (b)  $\text{NH}_3$  is added to  $\text{AgCl}$  (insoluble) .....
- (c)  $\text{KI}$  is added to  $\text{HgI}_2$  (insoluble) .....
- (d)  $\text{H}_2\text{O}$  is added  $\text{BiCl}_3$  (soluble) in  $\text{HCl}$  .....
- (e)  $\text{H}_2\text{O}$  is added to  $\text{SbCl}_3$  (soluble) in  $\text{HCl}$  .....

4. Consider following activity with salt  $X$



$X$  contains (A) ..... as acid radicals.

Solution of  $X$  is (B) .....

Formation of pink colour with phenolphthalein indicates that aqueous solution of  $X$  is (C) .....

Colourless solution is formed due to (D) .....

5.  $\text{MnO}_4^-/\text{H}^+$  is decolourised by radicals

- (i) .....
- (ii) .....
- (iii) .....

6. Two different test tubes contain  $\text{CH}_3\text{COO}^-$  and  $\text{S}_2\text{O}_3^{2-}$  (thiosulphate). Specify one reagent which can detect both. Reagent .....

|                                | Product | Colour |
|--------------------------------|---------|--------|
| I. $\text{S}_2\text{O}_3^{2-}$ | .....   | .....  |
| II. $\text{CH}_3\text{COO}^-$  | .....   | .....  |

7. Write the formulae of

- (a) Chromyl chloride .....
- (b) Brown-coloured complex (ring) in nitrate test .....
- (c)  $\text{AgCl}$  in the form of complex with aqueous  $\text{NH}_3$  .....

8. Brown-coloured ring is formed in nitrate test

- (a) Write EC. of iron in the complex .....
- (b) What is EAN of iron? .....

- (c) What is magnetic moment of iron? .....

- (d) What is charge on  $\text{NO}$ ? .....

9. Take solution oxalate in a test-tube and heat it strongly. Take a burning match-stick at the mouth of the test-tube. You observe that a gas is burning at mouth of the test tube but on further heating gas is put-off itself.

- (a) gas burns due to .....
- (b) gas is put-off due to .....

## Answers

- $\text{H}_3\text{O}^+$  and  $\text{Cl}^-$
- (i) White insoluble  
(ii) Blue soluble  
(iii) White soluble  
(iv) Violet insoluble  
(v) Brown ( $\text{I}_3^-$ ) soluble  
(vi) White soluble
- (a)  $\text{AgCl}$  changes to  $\text{K}[\text{Ag}(\text{CN})_2]$  (soluble)  
(b)  $\text{AgCl}$  change to  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  (soluble)  
(c)  $\text{HgI}_2$  changes to  $\text{K}_2\text{HgI}_4$  (soluble)  
(d)  $\text{BiCl}_3$  is hydrolysed to  $\text{BiOCl}$  (insoluble)  
(e)  $\text{SbCl}_3$  is hydrolysed to  $\text{SbOCl}$  (insoluble)
- (A)  $\text{CO}_3^{2-}$  (B) Basic (C) Alkaline  
(D) If  $\text{CO}_2$  ( $\text{CO}_3^{2-} + \text{dil. H}_2\text{SO}_4$ ) is passed into above pink-coloured solution,  $\text{HCO}_3^-$  formed decolourises it  

$$\text{CO}_3^{2-} + \text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{HCO}_3^-$$
- (i)  $\text{Fe}^{2+}$  (ii)  $\text{C}_2\text{O}_4^{2-}$  (iii)  $\text{NO}_2^-$   
There are so many others.
- Reagent  $\text{FeCl}_3$

|                                | Product                                                 | Colour      |
|--------------------------------|---------------------------------------------------------|-------------|
| I. $\text{S}_2\text{O}_3^{2-}$ | $[\text{Fe}(\text{S}_2\text{O}_3)_2]^-$                 | dark-violet |
| II. $\text{CH}_3\text{COO}^-$  | $[\text{Fe}_2(\text{OH})_2(\text{CH}_3\text{COO})_6]^+$ | blood dark  |

- (a)  $\text{CrO}_2\text{Cl}_2$  (b)  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  (c)  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$
- Fe is in (+1) state  
(a)  $[\text{Ar}] 4s^0 3d^7$ 

|                      |                      |            |            |            |
|----------------------|----------------------|------------|------------|------------|
| $\uparrow\downarrow$ | $\uparrow\downarrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ |
|----------------------|----------------------|------------|------------|------------|

  
(b)  $\text{EAN} = Z - (\text{O.N.}) + 2 \times (\text{ligands})$   

$$= 26 - 1 + 12 = 37$$
  
(c)  $= \sqrt{N(N+2)} = \sqrt{15} = 3.87 \text{ BM}$  due to three unpaired electrons.  
(d) +1
- (a) CO (b)  $\text{CO}_2$   
Note: CO (molar mass = 28) diffuses more rapidly than  $\text{CO}_2$  (molar mass = 44) hence, (CO) gas burns. After further heating  $\text{CO}_2$  goes upwards which puts off burning CO.

## Practice Exercise 1

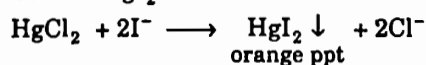
- Oil paintings turn blackish after sometime. What is the salt formed? Assume oil paint contains  $\text{Pb}^{2+}$ .
- A metallic statue under 'acid-rain' attack is turned bluish-green. What can be the probable metal and the ion formed?
- Potassium permanganate is purple in colour. On adding with  $\text{KOH}$ , it turns green. What is the compound formed?
- Aqueous solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  (orange) changes to yellow on adding alkali. Can you explain.
- $\text{FeCl}_3$  is yellow in aqueous solution but on passing  $\text{H}_2\text{S}$  gas, solution turns green. Explain.
- $\text{CO}_2$  and  $\text{SO}_2$  both turn lime water milky. How will you detect the presence if both are present in a mixture?
- Identify (A), (B) and (C).  
 $(\text{A}) + \text{dil. H}_2\text{SO}_4 \longrightarrow \text{brown colour vapours turning (KI + starch) paper blue.}$   
 $(\text{A}) + \text{NaOH} \xrightarrow{\Delta} \text{NH}_3(\text{g})$   
 $(\text{A}) \xrightarrow{\Delta} (\text{B})(\text{g}) + (\text{C})(\text{g}), (\text{but } (\text{C}) \text{ liquid at room temperature})$
- (A), (black) +  $\text{dil. H}_2\text{SO}_4 \longrightarrow (\text{B})(\text{g}) + (\text{C})$  (light green colour solution). Gas (B) turns lead acetate paper black. What are (A), (B) and (C)?
- $\text{NO}_2^-$  interferes in the 'Ring Test' of  $\text{NO}_3^-$ . Suggest a chemical method of removal of  $\text{NO}_2^-$ .
- $\text{I}^-$  also interferes in the 'Ring Test' of  $\text{NO}_3^-$ . Suggest a chemical reagent that can remove  $\text{I}^-$ .
- Arrange  $\text{AgF}$ ,  $\text{AgCl}$ ,  $\text{AgBr}$  and  $\text{AgI}$  in the increasing order of solubility in water.
- While testing oxalate, gas obtained burns with a blue flame initially but is put off instantly even as gas appears coming. Explain.
- Can you detect  $\text{Br}^-$  and  $\text{I}^-$  by 'Layer Test' if present together.
- Colourless solid (A)  $\xrightarrow{\Delta} (\text{B})(\text{g}) + (\text{C})(\text{g})$ . Aqueous solutions of (A) and (B) turn blue litmus red while that of (C) turns red litmus blue. Aqueous solutions of (A) and (B) also give white ppt with  $\text{AgNO}_3$  solution soluble in aqueous solution of (C). Identify (A), (B) and (C).

## Answers

- $\text{PbS}$
- Probable metal : Cu  
Salt formed :  $\text{Cu}^{2+}$
- $2\text{KMnO}_4 + 2\text{KOH} \longrightarrow 2\text{K}_2\text{MnO}_4 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$   
green
- $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \longrightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$   
orange
yellow
- $2\text{FeCl}_3 + \text{H}_2\text{S} \longrightarrow 2\text{FeCl}_2 + 2\text{HCl} + \text{S}$   
green
- Pass the mixture of gases first into acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution then into lime water.  
 \* If  $\text{K}_2\text{Cr}_2\text{O}_7$  solution turns green —  $\text{SO}_2$   
 \* If lime water turns milky —  $\text{CO}_2$
- (A) :  $\text{NH}_4\text{NO}_2$  (B) :  $\text{N}_2$  (C) :  $\text{H}_2\text{O}$
- (A) :  $\text{FeS}$  (B) :  $\text{H}_2\text{S}$  (C) :  $\text{FeSO}_4$
- Boil the mixture with  $\text{NH}_4\text{Cl}$ ,  $\text{NO}_2^-$  is decomposed as  $\text{N}_2$ :  

$$\text{NaNO}_2 + \text{NH}_4\text{Cl} \xrightarrow{\Delta} \text{NaCl} + \text{N}_2 \uparrow + 2\text{H}_2\text{O}$$

10.  $\text{HgCl}_2$  removes  $\text{I}^-$  as  $\text{HgI}_2$

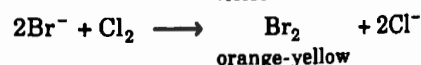
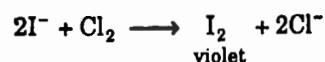


11.  $\text{AgI} < \text{AgBr} < \text{AgCl} < \text{AgF}$

12.  $\text{H}_2\text{C}_2\text{O}_4 \xrightarrow{\Delta} \text{H}_2\text{O}(l) + \text{CO}(g) + \text{CO}_2(g)$

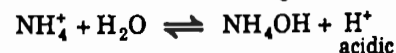
$\text{CO}$  burns with blue flame. It diffuses faster than  $\text{CO}_2$ . Once  $\text{CO}$  burns with blue flame, it is put off by  $\text{CO}_2$  which diffuses later.

13. Reducing power of  $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$ . Add  $\text{Cl}_2$  water and  $\text{CHCl}_3$  into mixture of  $\text{I}^-$  and  $\text{Br}^-$ .



$\text{Br}_2$  will also oxidise  $\text{I}^-$  to  $\text{I}_2$ . Thus, first there will be violet colour in  $\text{CHCl}_3$  layer. Extract aqueous layer (containing  $\text{Br}^-$ ) and repeat adding  $\text{Cl}_2$  water and  $\text{CHCl}_3$ . Orange-yellow colour in  $\text{CHCl}_3$  layer confirms  $\text{Br}^-$ .

14. (A) :  $\text{NH}_4\text{Cl}$  (B) :  $\text{HCl}$  (C) :  $\text{NH}_3$



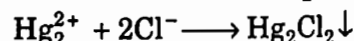
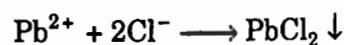
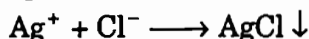
## Analysis of Basic (cation) Radicals

### Classification into Groups

Based on the values of solubility products ( $K_{sp}$ ), basic radicals are classified into groups summarised in Table 19.3

#### Group I

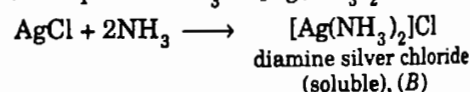
$\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}_2^{2+}$  are precipitated as insoluble chlorides on adding dil.  $\text{HCl}$  to aqueous solution. If no precipitate, this group is absent.



Precipitates are separated. Filtrate is for group II.

#### DEEP Focus

- $\text{PbCl}_2$  (A) is soluble in hot water and thus separated.
- $\text{AgCl}$  is soluble in aqueous  $\text{NH}_3$  as  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$



- $\text{Hg}_2\text{Cl}_2$  is blackened by  $\text{NH}_3$

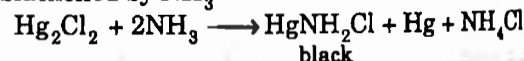
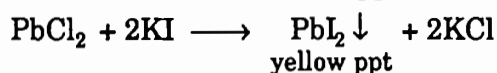
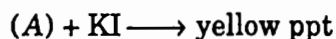


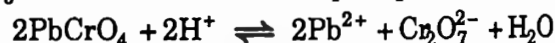
Table 19.3 Classification of Basic Radicals into Groups Based on  $K_{sp}$  Values

| Group    | Basic radicals                                                                                                                                              | Group reagent                                                                 | Precipitate as                                                          | Explanation                                                                                                                                                                                                                                                                                                  |
|----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|-------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| I        | $\text{Ag}^+$ , $\text{Hg}_2^{2+}$ (I), $\text{Pb}^{2+}$                                                                                                    | dil. $\text{HCl}$                                                             | chloride ( $\text{AgCl}$ , $\text{Hg}_2\text{Cl}_2$ , $\text{PbCl}_2$ ) | $K_{sp}$ values of chlorides are low, hence precipitated. Others have higher $K_{sp}$ values hence not precipitated.                                                                                                                                                                                         |
| II       | $\text{Cu}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Hg}_2^{2+}$ (II), $\text{Bi}^{3+}$ , $\text{Sb}^{3+}$ , $\text{Sn}^{2+}$ , $\text{As}^{3+}$ | $\text{H}_2\text{S}$ gas in presence of dil. $\text{HCl}$                     | sulphides ( $\text{CuS}$ , $\text{As}_2\text{S}_3$ etc)                 | $K_{sp}$ values of sulphides are low hence precipitated by low $[\text{S}^{2-}]$ ion. $\text{HCl}$ (with common $\text{H}^+$ ion) decreases ionisation of $\text{H}_2\text{S}$ which gives low $[\text{S}^{2-}]$ . Hence, II group is precipitated. Others with higher $K_{sp}$ values are not precipitated. |
| III      | $\text{Al}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Fe}^{3+}$                                                                                                      | $\text{NH}_4\text{OH}$ in presence of $\text{NH}_4\text{Cl}$                  | hydroxide, etc. $\text{Al}(\text{OH})_3$                                | $K_{sp}$ values of $\text{Al}(\text{OH})_3$ etc are low. $\text{NH}_4\text{Cl}$ (with common $\text{NH}_4^+$ ion) decrease ionisation of $\text{NH}_4\text{OH}$ giving low $[\text{OH}^-]$ . Hence, group III is precipitated.                                                                               |
| IV       | $\text{Zn}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Co}^{2+}$                                                                                   | $\text{H}_2\text{S}$ in ammoniacal medium                                     | sulphides ( $\text{ZnS}$ etc.)                                          | $K_{sp}$ values of sulphides of group IV are high hence precipitation takes place in higher $[\text{S}^{2-}]$ Basic medium increases ionisation of $\text{H}_2\text{S}$ , thus increasing $[\text{S}^{2-}]$ hence precipitation of group IV.                                                                 |
| V        | $\text{Ca}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Sr}^{2+}$                                                                                                      | $(\text{NH}_4)_2\text{CO}_3 + \text{NH}_4\text{Cl}$                           | carbonates ( $\text{CaCO}_3$ etc.)                                      | $K_{sp}$ values of carbonate are less than that of group VI ( $\text{Mg}^{2+}$ ) hence precipitation before $\text{Mg}^{2+}$ .                                                                                                                                                                               |
| VI       | $\text{Mg}^{2+}$ , ( $\text{Na}^+$ , $\text{K}^+$ ) also included                                                                                           | $\text{NH}_4\text{OH} + \text{Na}_2\text{HPO}_4$ (only for $\text{Mg}^{2+}$ ) | white ppt ( $\text{MgHPO}_4$ )                                          | —                                                                                                                                                                                                                                                                                                            |
| 0 (zero) | $\text{NH}_4^+$                                                                                                                                             | —                                                                             | —                                                                       | tested independently from original solution.                                                                                                                                                                                                                                                                 |

**$\text{Pb}^{2+}$  :** A : soluble  $\text{PbCl}_2$  (in hot water) solution.

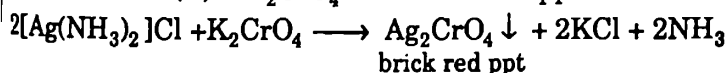
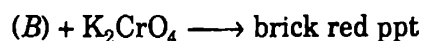
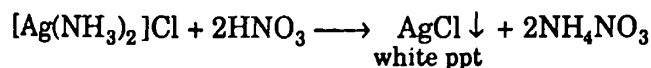
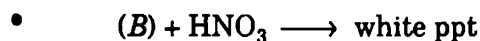
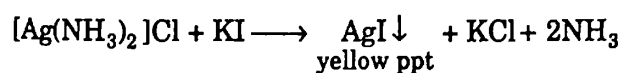


$\text{HNO}_3$  are  $\text{NaOH}$  dissolve the precipitate of  $\text{PbCrO}_4$

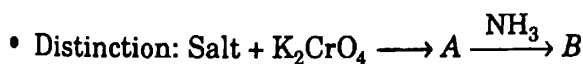
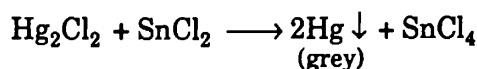
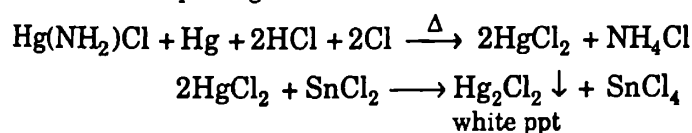
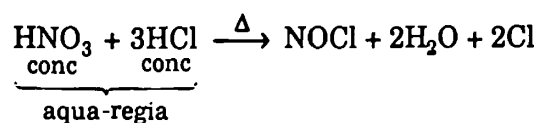


**$\text{Ag}^+$  :** B : soluble  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$

- (B) +  $\text{KI} \longrightarrow \text{yellow ppt}$



$\text{Hg}_2^{2+}$  : Black  $[\text{Hg}(\text{NH}_2)\text{Cl} + \text{Hg}] + \text{aqua-regia}$ , heat to dissolve

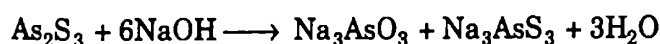
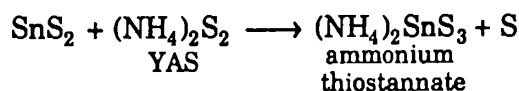
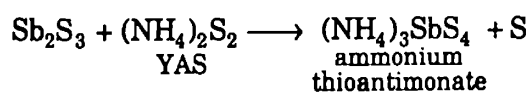
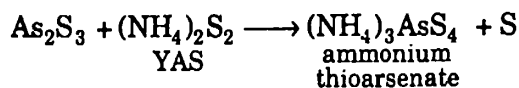


| $\text{Pb}^{2+}$                       | $\text{Hg}_2^{2+}$                       | $\text{Ag}^+$                               |
|----------------------------------------|------------------------------------------|---------------------------------------------|
| A : Yellow $\text{PbCrO}_4 \downarrow$ | Red $\text{Hg}_2\text{CrO}_4 \downarrow$ | Red $\text{Ag}_2\text{CrO}_4 \downarrow$    |
| B : no change                          | black $\text{Hg} \downarrow$             | dissolves as $[\text{Ag}(\text{NH}_3)_2]^+$ |

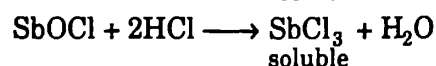
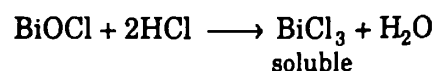
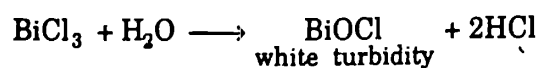
## Group II

Filtrate of group I + dil.  $\text{HCl} + \text{H}_2\text{O}$ . Pass  $\text{H}_2\text{S}$  gas  $\longrightarrow$

- yellow ppt —  $\text{CdS}$
- black ppt —  $\text{PbS}, \text{HgS}, \text{Bi}_2\text{S}_3, \text{CuS}$  (salt is blue)
- bright yellow ppt —  $\text{As}_2\text{S}_3$
- dark brown ppt —  $\text{SnS}$
- orange ppt —  $\text{Sb}_2\text{S}_3$
- $\text{As}_2\text{S}_3, \text{SnS}, \text{Sb}_2\text{S}_3$  (II B—Arsenic group) are soluble in yellow ammonium sulphide (YAS) or  $\text{NaOH}$ .



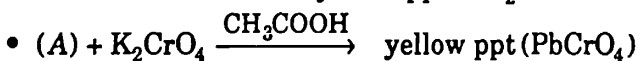
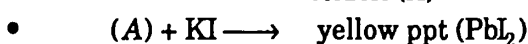
- $\text{PbS}, \text{CdS}, \text{HgS}, \text{Bi}_2\text{S}_3, \text{CuS}$  (II A—Copper group) are insoluble in YAS.
- If on dilution with  $\text{H}_2\text{O}$  (before passing  $\text{H}_2\text{S}$ ), there is white turbidity— $\text{Bi}^{3+}$  confirmed, or orange turbidity— $\text{Sb}^{3+}$  confirmed. Turbidity disappears on adding dil.  $\text{HCl}$ .



- $\text{PbS}, \text{CdS}, \text{CuS}, \text{Bi}_2\text{S}_3$  are soluble in  $\text{HNO}_3$  (1 : 1) while  $\text{HgS}$  is insoluble;  $\text{HgS}$ , however, is soluble in aqua regia.

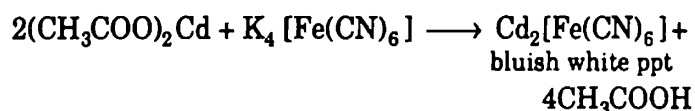
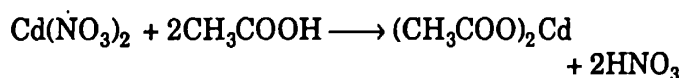
$\text{Pb}^{2+}$  :

- $\text{PbS}$  (black) is soluble in  $\text{HNO}_3$  (1 : 1)
- $3\text{PbS} + 8\text{HNO}_3 \longrightarrow 3\text{Pb}(\text{NO}_3)_2 + 2\text{NO} + 3\text{S} + 4\text{H}_2\text{O}$   
soluble (A)



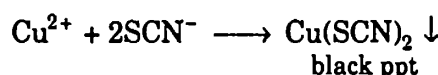
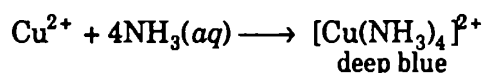
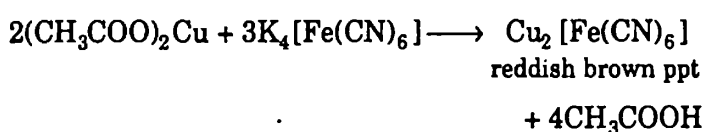
$\text{Cd}^{2+}$  :

- $3\text{CdS}$  (yellow) +  $8\text{HNO}_3 \xrightarrow{\Delta} 3\text{Cd}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O} + 3\text{S}$   
(B)
- $(B) + \text{CH}_3\text{COOH} + \text{K}_4[\text{Fe}(\text{CN})_6] \longrightarrow \text{bluish white ppt}$



$\text{Cu}^{2+}$  (salt is blue)

- $3\text{CuS}$  (black) +  $8\text{HNO}_3 \longrightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 3\text{S}$   
soluble (blue)  
(C)

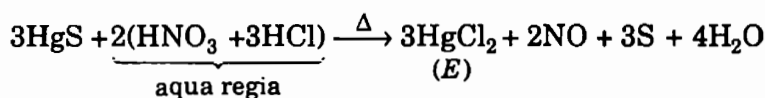


$\text{Bi}^{3+}$  :

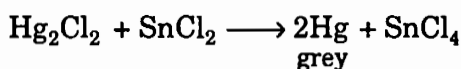
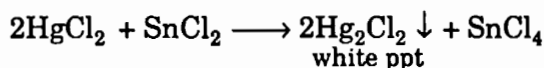
- $\text{Bi}_2\text{S}_3$  (black) +  $8\text{HNO}_3 \longrightarrow 2\text{Bi}(\text{NO}_3)_3 + 2\text{NO} + 4\text{H}_2\text{O} + 3\text{S}$   
(D)

- $(D) + \text{NH}_4\text{OH} \longrightarrow$  white ppt of  $\text{Bi}(\text{OH})_3$   
 $\text{Bi}(\text{NO}_3)_3 + 3\text{NH}_4\text{OH} \longrightarrow \text{Bi}(\text{OH})_3 + 3\text{NH}_4\text{NO}_3$   
 $\text{Bi}(\text{OH})_3 + \text{dil. HCl} \longrightarrow$  ppt dissolves forming  $\text{BiCl}_3$   
 $\text{BiCl}_3 + \text{Na}_2\text{SnO}_2 \xrightarrow{\text{NaOH}}$  black residue  
sodium stannite  
 $\text{BiCl}_3 + 6\text{NaOH} + 3\text{Na}_2\text{SnO}_2 \longrightarrow 3\text{Na}_2\text{SnO}_3 + 2\text{Bi} \downarrow$   
black  
 $+ 3\text{H}_2\text{O} + 6\text{NaCl}$

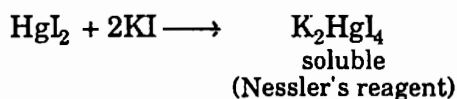
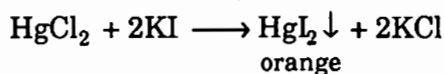
$\text{Hg}^{2+}$  :  $\text{HgS}$  (black) is soluble in aqua regia.



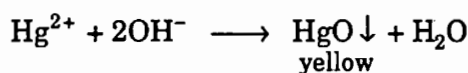
$(E) + \text{SnCl}_2 \longrightarrow$  white ppt changing to grey



$(E) + \text{KI} \longrightarrow$  orange ppt soluble in excess of KI



- $(E) + \text{NaOH}$  (in small amount)  $\longrightarrow$  brownish red ppt which changes to yellow on adding NaOH in stoichiometric amount.



### Group III

Boil off  $\text{H}_2\text{S}$  gas from the filtrate of group II. Add  $\text{NH}_4\text{Cl}$  and one drop of dil.  $\text{HNO}_3$ ; heat, cool and add  $\text{NH}_4\text{OH} \longrightarrow$  ppt

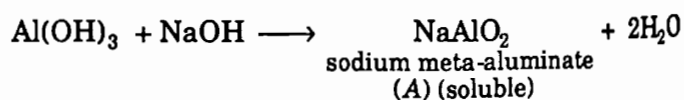
- Reddish brown ppt of  $\text{Fe}(\text{OH})_3$  if  $\text{Fe}^{3+}$  is present (salt is brown).
- Dirty green ppt of  $\text{Cr}(\text{OH})_3$  if  $\text{Cr}^{3+}$  is present (salt is green).
- White ppt of  $\text{Al}(\text{OH})_3$  if  $\text{Al}^{3+}$  is present (salt is colourless).

#### DEEP Focus

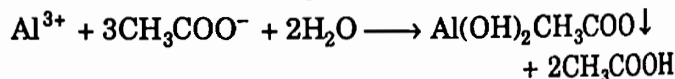
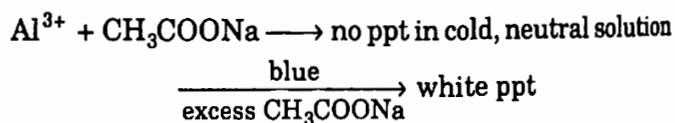
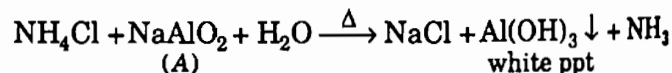
- dil.  $\text{HNO}_3$  is added to convert  $\text{Fe}^{2+}$  (light green) into  $\text{Fe}^{3+}$  (deep yellow).
- $\text{NH}_4\text{Cl}$  by common-ion effect decreases ionisation of  $\text{NH}_4\text{OH}$ .

$\text{Al}^{3+}$  :

- White ppt of  $\text{Al}(\text{OH})_3$  (salt is colourless) + NaOH solution (excess)  $\longrightarrow$  ppt dissolves forming  $\text{NaAlO}_2$ .

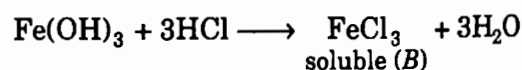


White ppt reappears if  $\text{NH}_4\text{Cl}$  is added into soluble meta-aluminate and boiled.



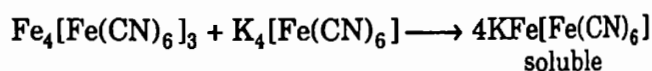
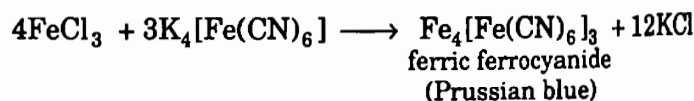
$\text{Fe}^{3+}$  :

$\text{Fe}(\text{OH})_3$  ppt are insoluble in NaOH but soluble in conc. HCl.

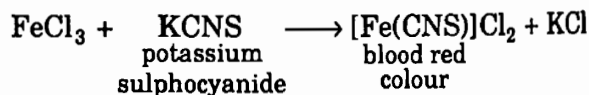


- $(B) + \text{CH}_3\text{COOH} + \text{K}_4[\text{Fe}(\text{CN})_6] \longrightarrow$  blue ppt  
potassium  
ferrocyanide

A large excess of the reagent dissolves it (Prussian blue) partly or entirely when an intense blue colour is obtained.

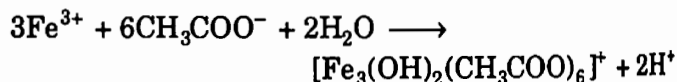


$(B) + \text{KCNS} \longrightarrow$  red colour



Actual composition of blood red colour is  $[\text{Fe}(\text{CNS})(\text{H}_2\text{O})_5]^{2+}$

- B + sodium acetate solution  $\longrightarrow$  a reddish brown colour

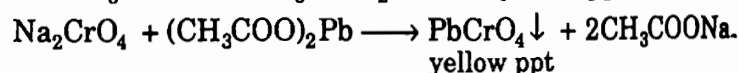
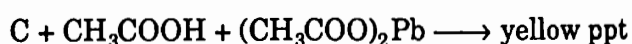
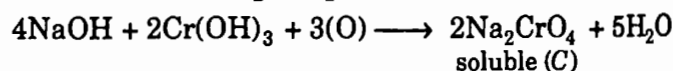
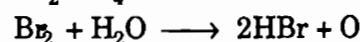


The reaction becomes complete only if the strong acid, which is formed, is removed by the addition of an excess of reagent, which acts as a buffer.

$\text{Fe}^{2+}$  does not give these tests, hence at the start of this group,  $\text{HNO}_3$  is added to convert  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$ .

$\text{Cr}^{3+}$  :

$\text{Cr}(\text{OH})_3$  (green ppt) is insoluble in NaOH but dissolves in presence of  $\text{Br}_2$  water (oxidising agent) giving yellow coloured  $\text{Na}_2\text{CrO}_4$  solution.

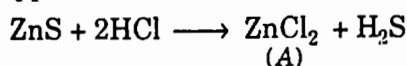


## Group IV

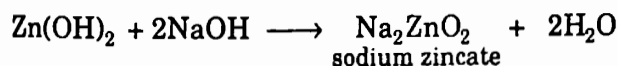
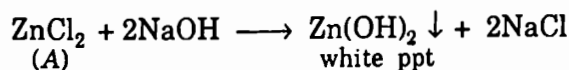
Filtrate of group III +  $\text{NH}_4\text{OH}$  +  $\text{NH}_4\text{Cl}$   $\xrightarrow{\Delta}$  pass  $\text{H}_2\text{S}$  gas  $\longrightarrow$

- white ppt (salt colourless) of  $\text{ZnS}$
- buff coloured ppt (salt light pink) of  $\text{MnS}$
- black ppt (salt green) of  $\text{NiS}$
- black ppt (salt dark blackish brown) of  $\text{CoS}$
- Ammoniacal medium increases ionisation of  $\text{H}_2\text{S}$ , hence higher  $[\text{S}^{2-}]$  will precipitate  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Mn}^{2+}$  as sulphides (having higher  $K_{sp}$  values)

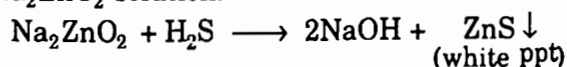
$\text{Zn}^{2+}$  :  $\text{ZnS}$  ppt (white) are soluble in dil  $\text{HCl}$ .



- (A) +  $\text{NaOH}$   $\longrightarrow$  white ppt soluble in excess of  $\text{NaOH}$ .



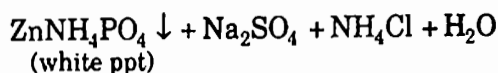
White ppt of  $\text{ZnS}$  reappears on passing  $\text{H}_2\text{S}$  into soluble  $\text{Na}_2\text{ZnO}_2$  solution.



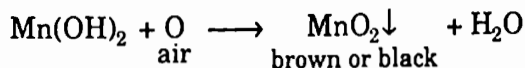
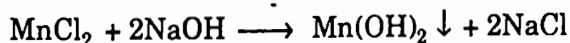
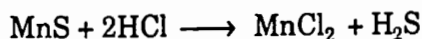
(A) +  $\text{CH}_3\text{COOH}$  +  $\text{K}_4[\text{Fe(CN)}_6]$   $\longrightarrow$  bluish white ppt



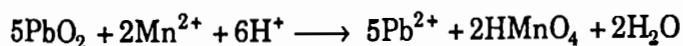
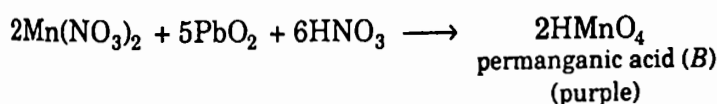
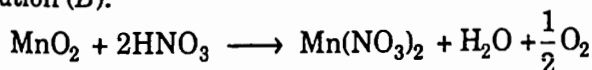
$\text{Zn}^{2+}$  salts form white ppt of  $\text{ZnNH}_4\text{PO}_4$  on reaction with  $\text{Na}_2\text{HPO}_4$  in basic buffer ( $\text{NH}_4\text{Cl}$  +  $\text{NH}_4\text{OH}$ )



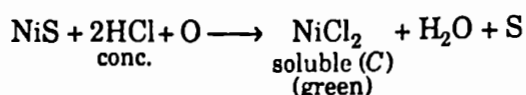
$\text{Mn}^{2+}$  :  $\text{MnS}$  (buff coloured ppt) are soluble in dil.  $\text{HCl}$  but addition of excess of  $\text{NaOH}$  gives  $\text{Mn(OH)}_2$  ppt which changes to brown/black by atmospheric  $\text{O}_2$ .



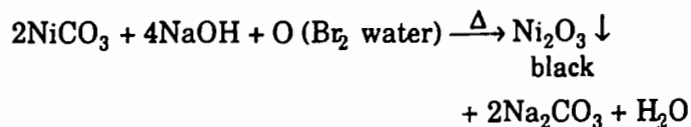
Dissolve  $\text{MnO}_2$  or  $\text{Mn(OH)}_2$  ppt into  $\text{HNO}_3$  and then add oxidising agent  $\text{KClO}_3$  or  $\text{PbO}_2$ ; heat to boil—purple solution (B).



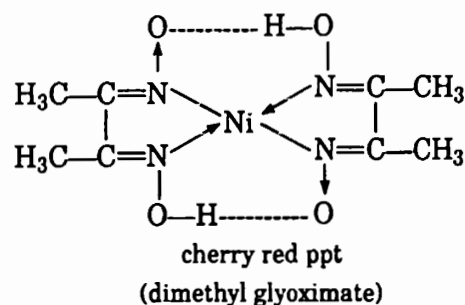
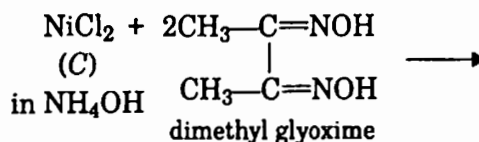
$\text{Ni}^{2+}$  :  $\text{NiS}$  (black ppt) is soluble in conc.  $\text{HCl}$  in presence of oxidising agent like  $\text{KClO}_3$ .



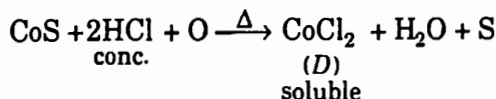
- (C) +  $\text{NaHCO}_3$  +  $\text{Br}_2$  water +  $\text{NaOH}$   $\xrightarrow{\Delta}$  black residue



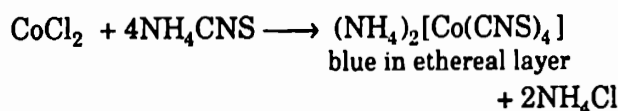
(C) +  $\text{NH}_4\text{OH}$  + dimethyl glyoxime  $\longrightarrow$  cherry red ppt



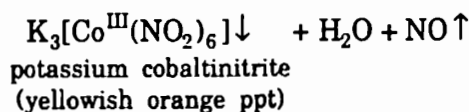
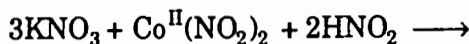
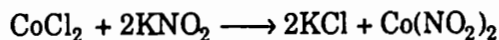
$\text{Co}^{2+}$  : Like  $\text{NiS}$ ,  $\text{CoS}$  (black ppt) is also soluble in conc.  $\text{HCl}$  in presence of oxidising agent  $\text{KClO}_3$



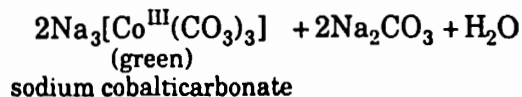
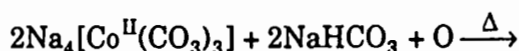
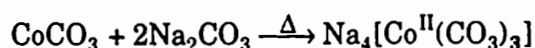
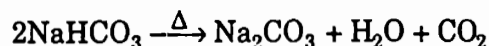
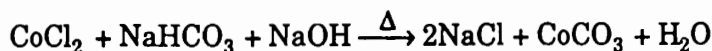
- (D) +  $\text{NH}_4\text{CNS}$  crystal + ether  $\longrightarrow$  blue colour in ethereal layer



- (D) +  $\text{CH}_3\text{COOH}$  +  $\text{KNO}_2$   $\longrightarrow$  yellowish orange ppt



- (D) +  $\text{NaOH}$  +  $\text{NaHCO}_3$  +  $\text{Br}_2$  water  $\xrightarrow{\Delta}$  green solution





## Group V

Filtrate of group IV  $\xrightarrow[\text{(ii) } \text{NH}_4\text{OH}, (\text{NH}_4)_2\text{CO}_3]{\text{(i) boil off H}_2\text{S}}$  white ppt

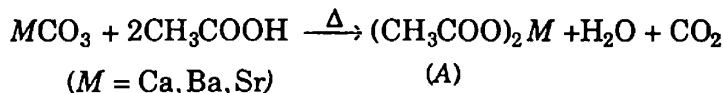
- $\text{BaCO}_3, \text{CaCO}_3, \text{SrCO}_3$  appear as white ppt
- **Flame test** Perform flame test with these group ppt

Green flame —  $\text{Ba}^{2+}$

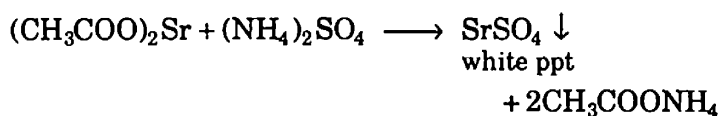
Crimson red —  $\text{Sr}^{2+}$

Brick red —  $\text{Ca}^{2+}$

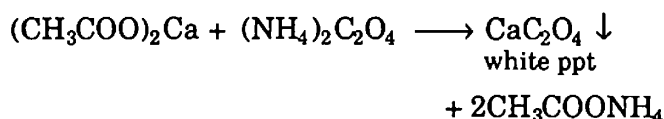
- Dissolve the ppt in  $\text{CH}_3\text{COOH}$ .



- $(\text{A}) + \text{K}_2\text{CrO}_4 \longrightarrow \text{yellow ppt } (\text{BaCrO}_4)$   
 $(\text{CH}_3\text{COO})_2\text{Ba} + \text{K}_2\text{CrO}_4 \longrightarrow \text{BaCrO}_4 \downarrow$   
yellow ppt  
+  $2\text{CH}_3\text{COOK}$
- $(\text{A}) + (\text{NH}_4)_2\text{SO}_4 \longrightarrow \text{white ppt } (\text{SrSO}_4)$

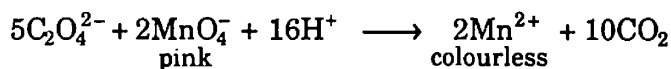
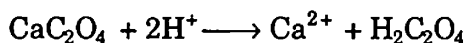


- $(\text{A}) + (\text{NH}_4)_2\text{C}_2\text{O}_4 \longrightarrow \text{white ppt } (\text{CaC}_2\text{O}_4)$



white ppt +  $\text{H}^+ + \text{MnO}_4^- \longrightarrow$  pink colour is discharged

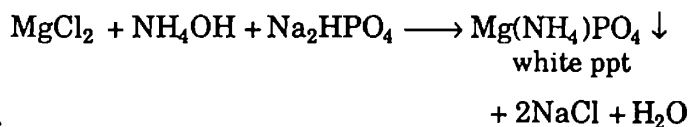
pink



+  $8\text{H}_2\text{O}$

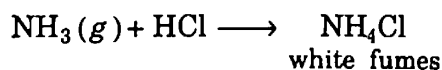
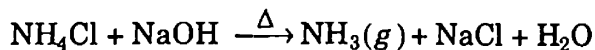
## Group VI ( $\text{Mg}^{2+}$ )

Filtrate of group V +  $\text{NH}_4\text{OH} + \text{Na}_2\text{HPO}_4 \longrightarrow$  a fine crystalline ppt on scratching the side of the test tube.

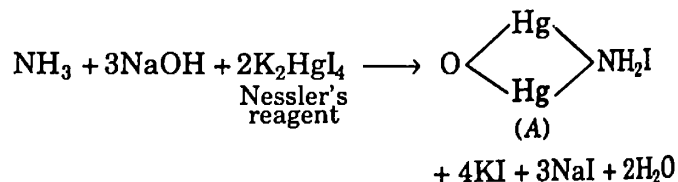
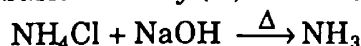


## Group Zero ( $\text{NH}_4^+$ )

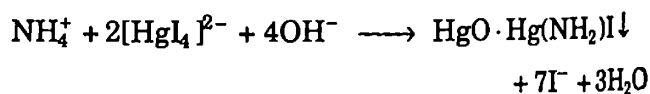
- Salt +  $\text{NaOH} \xrightarrow{\Delta}$  gas giving white fumes with  $\text{HCl}$



- Salt +  $\text{NaOH} \xrightarrow{\Delta}$  gas  $\xrightarrow{\text{add Nessler's reagent}}$  brown ppt or brown or yellow colouration (oxydimercuri ammonium iodide) called iodide of Millon's base (A). A is also called basic mercury (II) amido iodine.



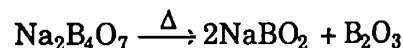
Above reaction can also be written as :



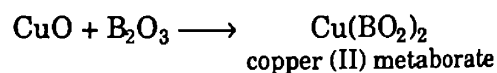
## Dry Tests

### Borax Bead Test

If borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  is heated on the platinum loop, a transparent colourless glass like bead of sodium metaborate ( $\text{NaBO}_2$ ) and boric anhydride ( $\text{B}_2\text{O}_3$ ) is formed.



Characteristics coloured beads are produced with salts of copper, iron, chromium, manganese, cobalt and nickel.



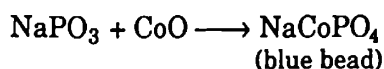
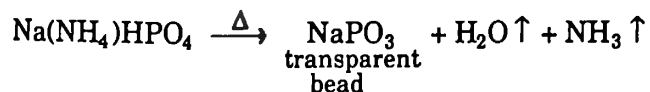
Results have been summarised in Table 19.4.

Table 19.4 **Colour in oxidising and Reducing Flames in Borax-Bead Test**

| Oxidising flame   |                 | Reducing flame |                  | Metal      |
|-------------------|-----------------|----------------|------------------|------------|
| Hot               | Cold            | Hot            | Cold             |            |
| Green             | Blue            | Colourless     | Opaque red-brown | Copper     |
| Yellowish-brown   | Yellow          | Green          | Green            | Iron       |
| Yellow            | Green           | Green          | Green            | Chromium   |
| Violet (amethyst) | Amethyst        | Colourless     | Colourless       | Manganese  |
| Blue              | Blue            | Blue           | Blue             | Cobalt     |
| Violet            | Reddish-brown   | Grey           | Grey             | Nickel     |
| Yellow            | Colourless      | Brown          | Brown            | Molybdenum |
| Rose-violet       | Rose-violet     | Red            | Violet           | Gold       |
| Yellow            | Colourless      | Yellow         | Yellowish-brown  | Tungsten   |
| Yellow            | Pale yellow     | Green          | Bottle-green     | Uranium    |
| Yellow            | Greenish-yellow | Brownish       | Emerald-green    | Vanadium   |
| Yellow            | Colourless      | Grey           | Pale violet      | Titanium   |
| Orange-red        | Colourless      | Colourless     | Colourless       | Cerium     |

## Microcosmic Salt Bead Test

A test similar to borax bead test is used for identification of coloured cations if microcosmic salt,  $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ , is used.



Results have been summarised in Table 19.5.

Table 19.5 Microcosmic Salt Bead Test

| Oxidising flame                                       | Reducing flame                                 | Metal     |
|-------------------------------------------------------|------------------------------------------------|-----------|
| Green when hot, blue when cold                        | Colourless when hot, red when cold             | Copper    |
| Yellowish-or reddish-brown when hot, yellow when cold | Yellow when hot, colourless to green when cold | Iron      |
| Green, hot and cold                                   | Green, hot and cold                            | Chromium  |
| Violet, hot and cold                                  | Colourless, hot and cold                       | Manganese |
| Blue, hot and cold                                    | Blue, hot and cold                             | Cobalt    |
| Brown, hot and cold                                   | Grey when cold                                 | Nickel    |
| Yellow, hot and cold                                  | Green when cold                                | Vanadium  |
| Yellow when hot, yellow-green when cold               | Green, hot and cold                            | Uranium   |
| Pale yellow when hot, colourless when cold            | Green when hot, blue when cold                 | Tungsten  |
| Colourless, hot and cold                              | Yellow when hot, violet when cold              | Titanium  |

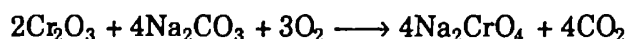
## Sodium Carbonate Bead Test

The sodium carbonate bead is prepared by fusing a small quantity of sodium carbonate on a platinum wire, loop in the Bunsen flame; a white, opaque bead is

produced. If this is moistened, dipped into a little  $\text{KNO}_3$  and then into a small quantity of a manganese salt (for example) and the whole heated in the oxidising flame, a green bead of sodium manganate ( $\text{Na}_2\text{MnO}_4$ ) is formed.



A yellow bead is obtained with chromium salt due to formation of sodium chromate ( $\text{Na}_2\text{CrO}_4$ )



## Flame Test

Paste of the salt and conc. HCl is taken into the lower oxidising zone and colour imparted to the flame by salts is observed; salts, particularly of group V ( $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ), are identified by colours of the flame and summarised in Table 19.6.

Table 19.6 Flame Tests

| Colour        | Cation                                                    |
|---------------|-----------------------------------------------------------|
| Golden yellow | $\text{Na}^+$                                             |
| Violet        | $\text{K}^+$                                              |
| Carmine-red   | $\text{Li}^+$                                             |
| Brick-red     | $\text{Ca}^{2+}$                                          |
| Apple-green   | $\text{Ba}^{2+}$ , $\text{Mo}^{2+}$                       |
| Green         | $\text{Cu}^{2+}$ , $(\text{BO}_3^{3-})$ , $\text{P}^{3+}$ |
| Crimson-red   | $\text{Sr}^{2+}$                                          |

The yellow colouration due to sodium masks that of potassium. In such cases view the flame through cobalt glass (Table 19.7), the yellow sodium colour is absorbed and the potassium flame appears crimson.

## Target Practice 2

1. One reagent can be used to detect more than one ion. Give colour of the precipitate/solution formed.

| Reagent                      | Colour of the precipitate with |                  |                  |
|------------------------------|--------------------------------|------------------|------------------|
|                              | $\text{Ag}^+$                  | $\text{Pb}^{2+}$ | $\text{Hg}^{2+}$ |
| (a) KI                       | .....                          | .....            | .....            |
| (b) $\text{K}_2\text{CrO}_4$ | .....                          | .....            | .....            |
| (c) HCl                      | .....                          | .....            | .....            |

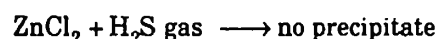
2. Thioacetamide ( $\text{CH}_3\text{CSNH}_2$ ) serves as a source of  $\text{H}_2\text{S}$ . Write reactions.

.....

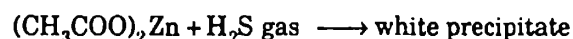
.....

3. Consider following experiments

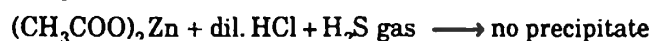
(i) Aqueous solution of



(ii) Aqueous solution of



(iii) Aqueous solution of



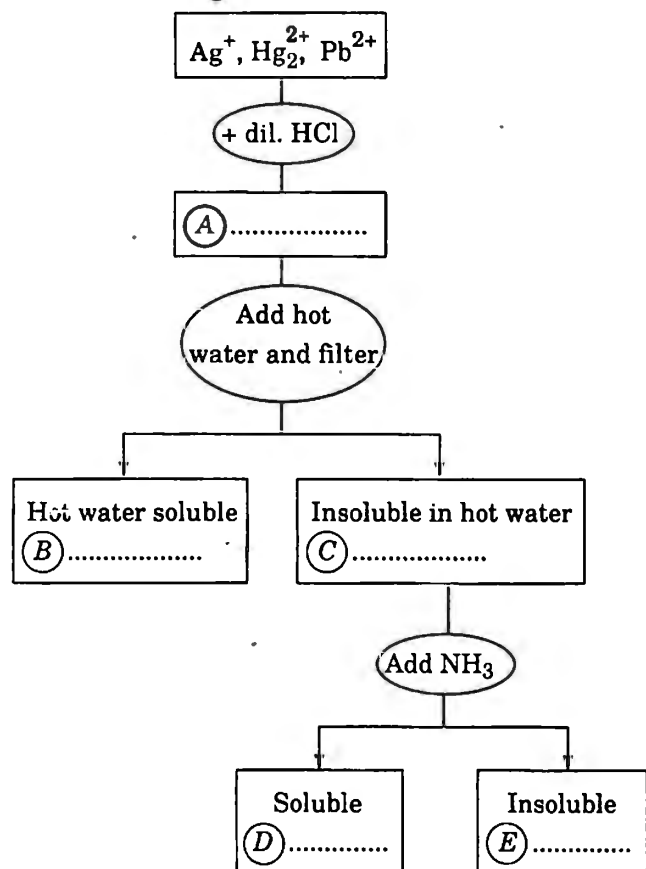
Observation in case of

(i) is due to .....

(ii) is due to .....

(iii) is due to .....

4. Write the compounds formed/ separated from a mixture containing  $\text{Ag}^+$ ,  $\text{Hg}_2^{2+}$  and  $\text{Pb}^{2+}$  in the following scheme.

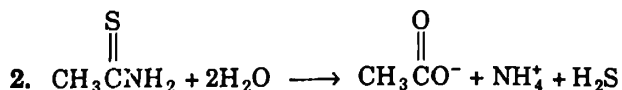


5. Write following reactions

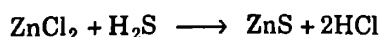
- Dissolution of  $\text{CuS}$  precipitate in dil.  $\text{HNO}_3$
- Dissolution of  $\text{HgS}$  precipitate in aqua regia
- Dissolution of  $\text{Ag}_2\text{S}_3$  in aqueous  $\text{NaOH}$
- Stannite  $[\text{Sn}(\text{OH})_3]^-$  ion disproportionates on long exposure to air

## Answers

| 1.  |                          | $\text{Ag}^+$                          | $\text{Pb}^{2+}$             | $\text{Hg}_2^{2+}$                                                                      |
|-----|--------------------------|----------------------------------------|------------------------------|-----------------------------------------------------------------------------------------|
| (a) | KI                       | $\text{AgI}$<br>(yellow)               | $\text{PbI}_2$<br>(yellow)   | $\text{HgI}_2$<br>orange soluble in<br>excess of KI forming<br>$\text{K}_2\text{HgI}_4$ |
| (b) | $\text{K}_2\text{CrO}_4$ | $\text{Ag}_2\text{CrO}_4$<br>black red | $\text{PbCrO}_4$<br>(yellow) | —                                                                                       |
| (c) | HCl                      | $\text{AgCl}$<br>(white)               | $\text{PbCl}_2$<br>(white)   | $\text{HgCl}_2$<br>(soluble)                                                            |



3. (i)  $\text{ZnS}$  is not precipitated in presence of  $\text{HCl}$  which is formed in following reaction :



6. Filtrate of group II has been given to you for analysis of group III (which may contain  $\text{Fe}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Al}^{3+}$ ). Mention systematic steps you would follow

Step I : .....

Step II : .....

Step III : .....

7. Two students (X and Y) have salts with common cation  $\text{Fe}^{2+}$  but different anion. Each of them dissolved the salt in water, added dil.  $\text{HCl}$ , boiled and added  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ .  
Student X : Light green precipitate.

Student Y : Brown precipitate.

Anion in X can be .....

Anion in Y can be .....

Light-green precipitate in X is due to .....

Brown precipitate in Y is due to .....

8. Give the reagents to identify  $\text{Fe}^{3+}$

(I) .....

(II) .....

(III) .....

9. A reagent can identify  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$ ; reagent is ..... and coloured formed with

(a)  $\text{Fe}^{3+}$  .....

(b)  $\text{Zn}^{2+}$  .....

(c)  $\text{Cd}^{2+}$  .....

(d)  $\text{Cu}^{2+}$  .....

10. Write the names of reagents to identify

(a)  $\text{Co}^{2+}$  .....

(b)  $\text{Ni}^{2+}$  .....

11.  $\text{Mn}^{2+}$  is identified by its oxidation to a salt giving pink colour in solution.

(a) Pink colour is due to formation of .....

(b) Oxidising agent used is .....

(c) Oxidised  $\text{Mn}^{2+}$  changes to ..... by  $\text{KOH}$ .

12.  $\text{KCNS}$  can identify following basic radicals

(I) .....

(II) .....

(III) .....

(ii)  $\text{CH}_3\text{COOH}$  does not dissolve  $\text{ZnS}$  which remains insoluble.

(iii) Medium is  $\text{HCl}$  and  $\text{ZnS}$  is dissolved.

4. (A) :  $\text{AgCl}$ ,  $\text{PbCl}_2$ ,  $\text{Hg}_2\text{Cl}_2$  (B) :  $\text{PbCl}_2$

(C) :  $\text{AgCl}$ ,  $\text{Hg}_2\text{Cl}_2$  (D) :  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$

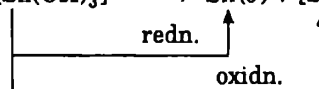
(E) :  $\text{HgNH}_2\text{Cl} + \text{Hg}$

5. (a)  $3\text{CuS} + 8\text{HNO}_3 \longrightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O} + 3\text{S}$

(b)  $3\text{HgS} + 2(\text{HNO}_3 + 3\text{HCl}) \xrightarrow{\Delta} 3\text{HgCl}_2 + 2\text{NO} + 3\text{S} + 4\text{H}_2\text{O}$   
aqua regia

(c)  $\text{As}_2\text{S}_3 + 6\text{NaOH} \longrightarrow \text{Na}_3\text{AsO}_3 + \text{Na}_3\text{AsS}_3 + 3\text{H}_2\text{O}$

(d)  $2[\text{Sn}(\text{OH})_3]^- \longrightarrow \text{Sn(s)} + [\text{Sn}(\text{OH})_6]^{2-}$



6. Step I : Boil off  $\text{H}_2\text{S}$

Step II : Add a drop of  $\text{HNO}_3$  (to oxidise  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ )

Step III : Add  $\text{NH}_4\text{Cl}$  boil, cool and add  $\text{NH}_4\text{OH}$ .

7. Anion in X can be all soluble anions except  $\text{NO}_3^-$ .

Anion in Y can be  $\text{NO}_3^-$

Light green precipitate in X due to  $\text{Fe}(\text{OH})_2$ .

Light green precipitate in Y is due to  $\text{Fe}(\text{OH})_3$ .

( $\text{HNO}_3$  formed in Y oxidises  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  hence,  $\text{Fe}(\text{OH})_3$  is formed)

8. I :  $\text{K}_4\text{Fe}(\text{CN})_6$  II :  $\text{KCNS}$  III :  $\text{CH}_3\text{COO}^-$

9. Reagent :  $\text{K}_4[\text{Fe}(\text{CN})_6]$

(a)  $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$  Prussian blue

(b)  $\text{Zn}_2[\text{Fe}(\text{CN})_6]$  bluish white  
(c)  $\text{Cd}_2[\text{Fe}(\text{CN})_6]$  bluish white  
(d)  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$  reddish brown

10. (a)  $\text{NH}_4\text{CNS}$   
(b) dimethyl glyoxime (DMG) in  $\text{NH}_4\text{OH}$ /alcoholic solution.

11. (a)  $\text{MnO}_4^-$   
(b)  $\text{Br}_2$  water or  $\text{PbO}_2/\text{H}^+$   
(c)  $\text{K}_2\text{MnO}_4$  (green)

12. I :  $\text{Fe}^{3+}$  II :  $\text{Co}^{2+}$  III :  $\text{Cu}^{2+}$

## Practice Exercise 2

1. Identify (A), (B), (C) and (D) in the following :  
Colourless salt (A) + conc.  $\text{H}_2\text{SO}_4 \longrightarrow$  brown fumes intensified on adding Cu turnings.

Aqueous solution (A) + Cu  $\longrightarrow$  blue coloured solution (B) and metal (C).

Aqueous solution (A) + HCl  $\longrightarrow$  white ppt soluble in aq. aous  $\text{NH}_3$  forming (D)

2. Colourless salt (A)  $\xrightarrow{\text{dil. HCl}}$  white ppt (B)  
soluble in  $\text{H}_2\text{O}$  soluble in hot water

(i)  $\text{FeSO}_4$   
(ii) conc.  $\text{H}_2\text{SO}_4$   
brown colour ring (D)  
yellow ppt (C)

Identify (A), (B), (C) and (D).

3. Salt (A) makes part of electrode and is insoluble in water. (A) is blackened by  $\text{NH}_3$  forming (B). (B) is soluble in aqua regia forming (C). (C) gives orange ppt with KI but ppt dissolves in excess of KI forming (D). Identify (A), (B), (C) and (D).

4. Identify (A), (B), (C) and (D) and explain reactions.

(A) (green coloured salt) +  $\text{K}_2\text{Cr}_2\text{O}_7$  + conc.  $\text{H}_2\text{SO}_4 \xrightarrow{\Delta}$  (B)

(B) (reddish brown gas) + NaOH  $\longrightarrow$  (C) (yellow coloured solution)

(C) +  $(\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}}$  (D) (yellow ppt)

(A) + NaOH +  $\text{Br}_2$  water  $\xrightarrow{\Delta}$  (C)

(C) +  $(\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}}$  (D)

5. Light green solution of (A) does not give blue coloured ppt with  $\text{K}_4[\text{Fe}(\text{CN})_6]$  but on adding a drop of  $\text{HNO}_3$ , blue ppt (B) appears. However, (A) gives blue colour (C) with  $\text{K}_3[\text{Fe}(\text{CN})_6]$ . Explain the formation of (B) and (C). Identify (A) if it, also gives white ppt with  $\text{AgNO}_3$  solution.

6. (A) (yellow coloured solution) changes to light green coloured solution (B) on passing  $\text{H}_2\text{S}$  gas. (A) and (B) both give white ppt with  $\text{BaCl}_2$  solution, insoluble in conc. HCl. A gives blue coloured ppt (C) with  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , (B) does not. What are (A), (B) and (C)?

7. (A) (colourless)  $\xrightarrow{\Delta}$  (B) (residue) + (C) (gas) + (D) (gas)

$\downarrow \text{H}_2\text{O}$   
solution of (B)  $\xrightarrow{(D)}$  milky

A gives brick red colour in flame and decolourises  $\text{MnO}_4^-/\text{H}^+$ . Gas (C) burns with blue flame. Identify (A), (B), (C) and (D).

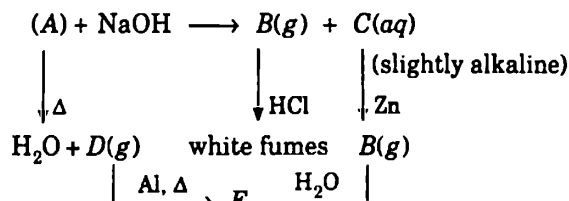
8.  $\text{MCl}_2 + \text{K}_2\text{CrO}_4 \longrightarrow$  Yellow ppt

What can be  $\text{MCl}_2$

- (a) if it is soluble in hot water?  
(b) if it gives green colour in flame?

9.  $\text{CaSO}_4$  is insoluble but is not precipitated when excess of  $(\text{NH}_4)_2\text{SO}_4$  is added to  $\text{CaCl}_2$ ; explain.

10. Identify (A), (B), (C), (D) and (E).



11. A (orange)  $\xrightarrow{\Delta}$  B(g) + residue (C) (green) +  $\text{H}_2\text{O}$

$\downarrow \text{NaOH}$   
 $\downarrow \Delta$   
 $D(g) \xrightarrow{\text{HCl}}$  white fumes

$B(g) \xrightarrow[\Delta]{\text{Al}}$  (E)  $\xrightarrow{\text{H}_2\text{O}}$  gas (B)

residue (C)  $\xrightarrow{\text{conc. HCl}}$  (F)  $\xrightarrow[\Delta]{\text{NaOH, H}_2\text{O}_2}$  G (yellow)  
 $\xrightarrow[\text{(CH}_3\text{COO)}_2\text{Pb}]{\text{CH}_3\text{COOH}}$  H (yellow)

Identify (A) to (H) and explain reactions.

12. Colourless salt (A) gives apple green flame with conc. HCl. (A) on reaction with dil.  $\text{H}_2\text{SO}_4$  gives light brown fumes (D) turning KI-starch paper blue.

(A) +  $\text{CH}_3\text{COOH} + \text{K}_2\text{CrO}_4 \longrightarrow$  yellow ppt (B)

(A) +  $\text{H}_2\text{SO}_4 \longrightarrow$  white ppt (C) + (D)

(D) +  $\text{CH}_3\text{NH}_2 \longrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} + \text{gas (E)}$

(E) + Mg  $\xrightarrow{\Delta}$  (F)

(F) +  $\text{H}_2\text{O} \longrightarrow \text{NH}_3$

Identify (A) to (F) and explain reactions.

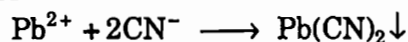
## Answers

- (A):  $\text{AgNO}_3$  (B):  $\text{Cu(NO}_3)_2$  (C):  $\text{Ag}$  (D):  $[\text{Ag(NH}_3)_2]\text{Cl}$
- (A):  $\text{Pb(NO}_3)_2$  (B):  $\text{PbCl}_2$  (C):  $\text{PbI}_2$   
(D):  $[\text{Fe(H}_2\text{O)}_5\text{NO}]^{2+}$
- (A):  $\text{Hg}_2\text{Cl}_2$  (calomel) (B):  $(\text{HgNH}_2\text{Cl} + \text{Hg})$   
(C):  $\text{HgCl}_2$  (D):  $\text{K}_2\text{HgI}_4$
- (A):  $\text{CrCl}_3$  (B):  $\text{CrO}_2\text{Cl}_2$  (by chromyl-chloride test of  $\text{Cl}^-$ )  
(C):  $\text{Na}_2\text{CrO}_4$  (D):  $\text{PbCrO}_4$
- (A):  $\text{FeCl}_2$  (B):  $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$  Prussian blue,  
(C):  $\text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ , Turnbull's blue
- (A):  $\text{FeCl}_3$  (B):  $\text{FeCl}_2$  (C):  $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ , Prussian blue
- (A):  $\text{CaC}_2\text{O}_4$  (B):  $\text{CaO}$  (C):  $\text{CO}$  (D):  $\text{CO}_2$
- (a)  $\text{PbCl}_2$  (b)  $\text{BaCl}_2$
- $\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4 \longrightarrow (\text{NH}_4)_2[\text{Ca(SO}_4)_2]$   
soluble
- (A):  $\text{NH}_4\text{NO}_2$  (B):  $\text{NH}_3$  (C):  $\text{NaNO}_2$  (D):  $\text{N}_2$   
(E):  $\text{AlN}$
- (A):  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (B):  $\text{N}_2$  (C):  $\text{Cr}_2\text{O}_3$  (D):  $\text{NH}_3$   
(E):  $\text{AlN}$  (F):  $\text{CrCl}_3$  (G):  $\text{Na}_2\text{CrO}_4$ , (H):  $\text{PbCrO}_4$
- (A):  $\text{Ba(NO}_3)_2$  (B):  $\text{BaCrO}_4$  (C):  $\text{BaSO}_4$  (D):  $\text{HNO}_2$   
(E):  $\text{N}_2$  (F):  $\text{Mg}_3\text{N}_2$

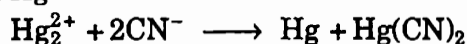
## One Reagent For Testing Different Ions

### 1. KCN

(a)  $\text{Pb}^{2+}$ :  $\text{Pb}^{2+}$  salts form white precipitate of  $\text{Pb(CN)}_2$  with KCN which is insoluble in excess of KCN.

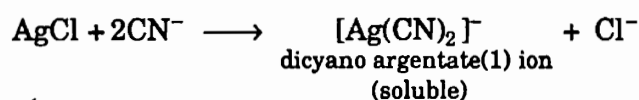


(b)  $\text{Hg}_2^{2+}$ :  $\text{Hg}_2^{2+}$  salts form soluble  $\text{Hg(CN)}_2$  and a precipitate of Hg

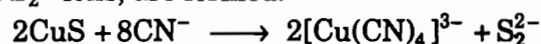


Above reaction is an example of disproportionation reaction.

(c)  $\text{Ag}^+$ :  $\text{CN}^-$  dissolves insoluble  $\text{AgCl}$  forming soluble  $[\text{Ag(CN)}_2]^-$

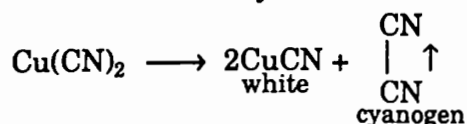
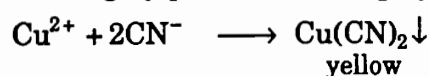


(d)  $\text{Cu}^{2+}$ : KCN dissolves the precipitate of  $\text{CuS}$ , when colourless tetracyanocuprate(I),  $[\text{Cu(CN)}_4]^{3-}$ , and disulphide  $\text{S}_2^{2-}$  ions, are formed.

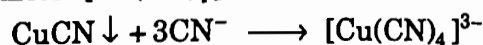


This is an oxidation-reduction process.  $\text{Cu}^{2+}$  is reduced to  $\text{Cu}^+$  and sulphur is oxidised coupled with formation of a complex.

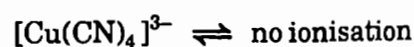
Soluble  $\text{Cu}^{2+}$  salts react with KCN forming yellow precipitate of copper(II) cyanide,  $\text{Cu(CN)}_2$  which quickly decomposes into white precipitate of copper(I) cyanide,  $\text{CuCN}$ , and a highly poisonous,  $(\text{CN})_2$ , cyanogen gas



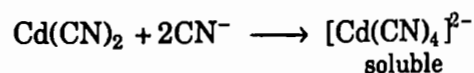
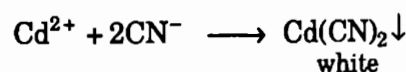
Excess of KCN dissolves the precipitate of  $\text{CuCN}$  forming colourless  $[\text{Cu(CN)}_4]^{3-}$



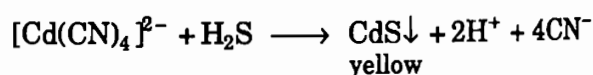
The complex is so stable that no precipitate of  $\text{CuS}$  is formed on passing  $\text{H}_2\text{S}$  gas



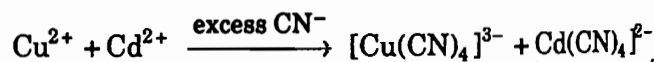
(e)  $\text{Cd}^{2+}$ :  $\text{Cd}^{2+}$  salts form white precipitate of  $\text{Cd(CN)}_2$  white dissolves in excess of KCN forming soluble tetracyanocadmate(II) ions



$[\text{Cd(CN)}_4]^{2-}$  is unstable forming free  $\text{Cd}^{2+}$  which is precipitate as  $\text{CdS}$  (yellow) on passing  $\text{H}_2\text{S}$  gas



Thus, mixture of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  can be identified by complex formation with  $\text{CN}^-$  and then passing  $\text{H}_2\text{S}$  gas.



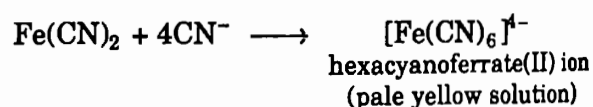
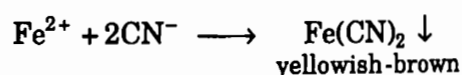
Yellow precipitate

Yellow ppt  $\xleftarrow{\text{H}_2\text{S}}$

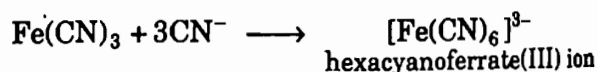
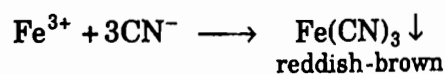
(a) confirms  $\text{Cd}^{2+}$  if original solution is colourless

(b) confirms  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  both if original solution is blue.

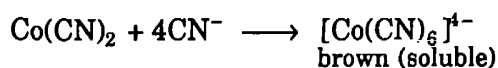
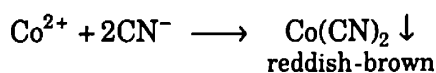
(f)  $\text{Fe}^{2+}$ : KCN forms yellowish-brown precipitate of  $\text{Fe(CN)}_2$  with  $\text{Fe}^{2+}$ , which dissolves in excess of KCN forming  $\text{K}_4[\text{Fe(CN)}_6]$  a pale yellow coloured solution.



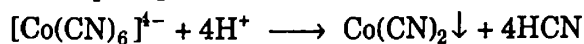
(g)  $\text{Fe}^{3+}$ : KCN forms reddish-brown precipitate of  $\text{Fe(CN)}_3$  with  $\text{Fe}^{3+}$ , which dissolves in excess of KCN due to formation of  $\text{K}_3[\text{Fe(CN)}_6]$  — a yellow coloured solution



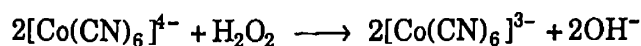
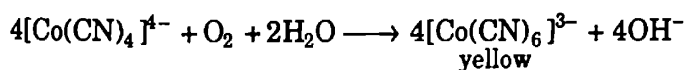
(h)  $\text{Co}^{2+}$  : KCN forms reddish-brown precipitate of  $\text{Co}(\text{CN})_2$  with  $\text{Co}^{2+}$  ions; precipitate dissolves in excess of KCN forming a brown solution of  $\text{K}_4[\text{Co}(\text{CN})_6]$



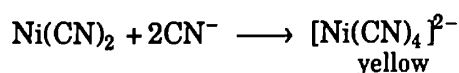
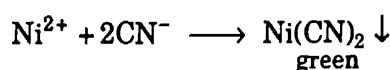
If dilute/cold HCl is added  $\text{Co}(\text{CN})_2$  reappears as reddish-brown precipitate



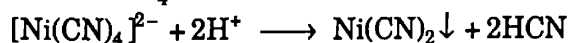
Brown solution of  $\text{K}_4[\text{Co}(\text{CN})_6]$  changes to yellow on boiling in air or by addition of  $\text{H}_2\text{O}_2$ .



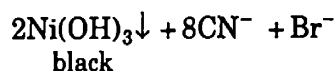
(i)  $\text{Ni}^{2+}$  KCN forms green precipitate of  $\text{Ni}(\text{CN})_2$  with  $\text{Ni}^{2+}$  salts; precipitate dissolves in excess of KCN forming a yellow coloured solution of  $[\text{Ni}(\text{CN})_4]^{2-}$ .



In presence of dil. HCl,  $\text{Ni}(\text{CN})_2$  is again precipitated from soluble  $[\text{Ni}(\text{CN})_4]^{2-}$ .

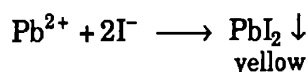


A black precipitate of  $\text{Ni}(\text{OH})_3$  is formed if soluble yellow solution of  $[\text{Ni}(\text{CN})_4]^{2-}$  is heated with sodium hypobromite solution



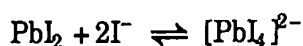
## 2. KI

(a)  $\text{Pb}^{2+}$  : Yellow precipitates of lead iodide are formed.



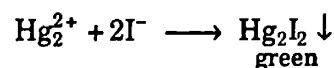
The precipitate is moderately soluble in boiling water to yield a colourless solution, from which it separates as golden yellow plates on cooling.

An excess of a more concentrated solution (6 M) of the reagent dissolves the precipitate and tetraiodoplumbate(II) ions are formed.

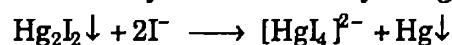


The action is reversible, on diluting with water the precipitate reappears.

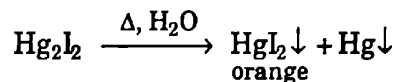
(b)  $\text{Hg}_2^{2+}$  (Mercurous ion) : Potassium iodide gives green precipitate of  $\text{Hg}_2\text{I}_2$  (mercury(I) iodide or mercurous iodide)



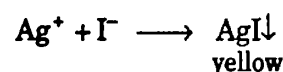
If excess of KI is added, a disproportionation reaction takes place, soluble tetraiodo mercurate(II) ions and a black precipitate of finely divided mercury being formed



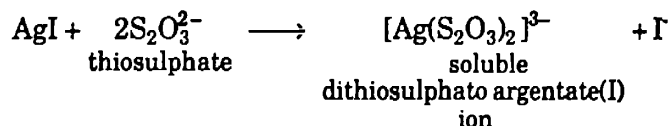
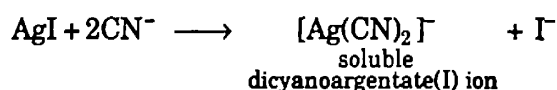
Disproportionation of  $\text{Hg}_2\text{I}_2$  also takes place to  $\text{HgI}_2$  and Hg on boiling it with  $\text{H}_2\text{O}$



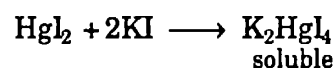
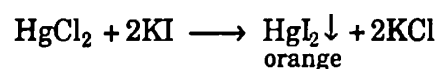
(c)  $\text{Ag}^+$  : KI gives yellow precipitate AgI with  $\text{Ag}^+$  ions.



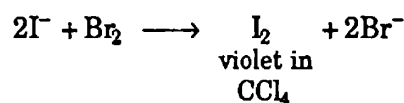
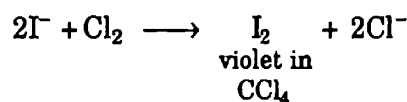
The precipitate is soluble in dilute or concentrated ammonia, but dissolves readily in KCN and in  $\text{Na}_2\text{S}_2\text{O}_3$



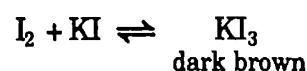
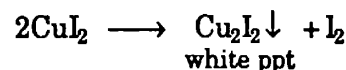
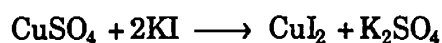
(d)  $\text{Hg}^{2+}$  (Mercuric ion) :  $\text{Hg}^{2+}$  gives orange precipitate of  $\text{HgI}_2$  with KI. Precipitate dissolves in excess of KI forming  $[\text{HgI}_4]^{2-}$



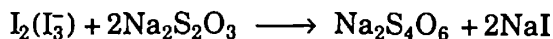
(e) KI is oxidised by  $\text{Cl}_2$  or  $\text{Br}_2$  forming  $\text{I}_2$  which appears as violet colour in  $\text{CCl}_4$  or  $\text{CHCl}_3$  layer



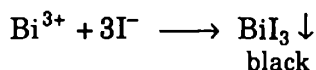
(f)  $\text{Cu}^{2+}$  :  $\text{Cu}^{2+}$  ( $\text{CuSO}_4$ ) gives white precipitates of  $\text{Cu}_2\text{I}_2$  along with  $\text{I}_2$  which gives dark brown coloured solution



If  $\text{Na}_2\text{S}_2\text{O}_3$  (sodium thiosulphate-hypo) is added,  $\text{I}_2$  disappears and white precipitate of  $\text{Cu}_2\text{I}_2$  appears



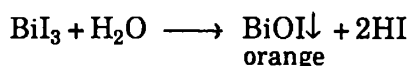
(g)  $\text{Bi}^{3+}$ : KI when added dropwise gives black precipitate of  $\text{BiI}_3$



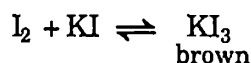
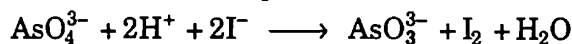
The precipitate dissolves readily in excess reagent forming  $[\text{BiI}_4]^-$  — orange coloured



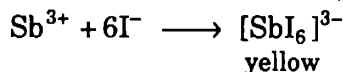
When diluted with  $\text{H}_2\text{O}$ , the above reaction is reversible forming  $\text{BiI}_3$  (black). Heating the precipitate with  $\text{H}_2\text{O}$ , it turns orange due to the formation of bismuthyl iodide.



(h) **Arsenate(V)  $\text{AsO}_4^{3-}$** : Arsenate(V) ions oxidise  $\text{I}^-$  to  $\text{I}_2$  in acidic medium which appears as brown coloured solution due to formation of  $\text{I}_3^-$



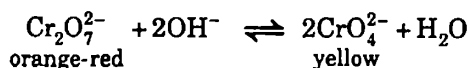
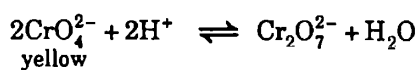
(i) **Antimony ( $\text{Sb}^{3+}$ )**: KI form yellows coloured solution with  $\text{Sb}^{3+}$  due to formation of  $[\text{SbI}_6]^{3-}$ .



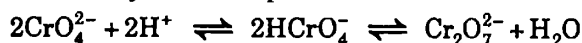
### 3. $\text{K}_2\text{CrO}_4$

#### DEEP Focus

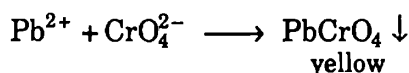
The metallic chromates are usually coloured solids, yielding yellow solution when soluble in water. In the presence of dilute mineral acids, chromates are converted into dichromates which yield orange-red aqueous solution. In alkali solution, dichromates change to chromate.



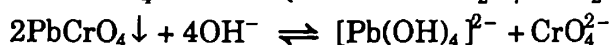
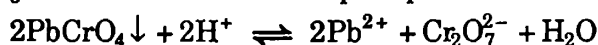
The reaction may also be expressed as :



(a)  $\text{Pb}^{2+}$ :  $\text{K}_2\text{CrO}_4$  gives yellow precipitate of  $\text{PbCrO}_4$  on reaction of  $\text{Pb}^{2+}$  salts after acidification with  $\text{CH}_3\text{COOH}$

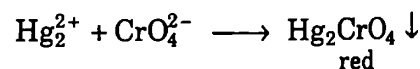


$\text{HNO}_3$  or  $\text{NaOH}$  dissolves the precipitate

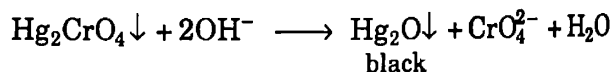


Both reactions are reversible; by buffering the solution with  $\text{NH}_3(\text{aq})$  or  $\text{CH}_3\text{COOH}$  respectively,  $\text{PbCrO}_4$  reprecipitates.

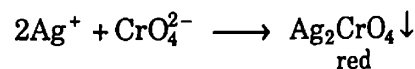
(b)  $\text{Hg}_2^{2+}$  (**Mercurous ion**):  $\text{Hg}_2^{2+}$  salts form red crystalline precipitate of  $\text{Hg}_2\text{CrO}_4$  (mercury(I) chromate)



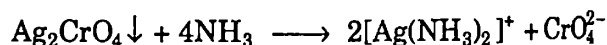
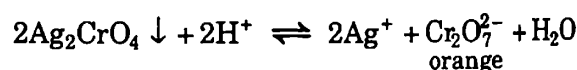
$\text{NaOH}$  turns the precipitate into black mercury(I) oxide :



(c)  $\text{Ag}^+$ :  $\text{Ag}^+$  salts form red precipitate of  $\text{Ag}_2\text{CrO}_4$  (silver(I) chromate)

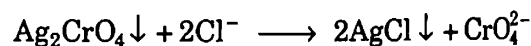


The precipitate is soluble in dilute  $\text{HNO}_3$  and in  $\text{NH}_3(\text{aq})$  solution.

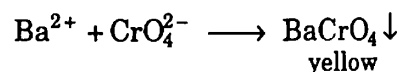


The acidified solution turns to orange because of the formation of  $\text{Cr}_2\text{O}_7^{2-}$ .

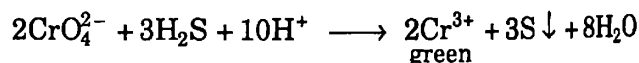
$\text{HCl}$  converts the precipitate into  $\text{AgCl}$  (white)



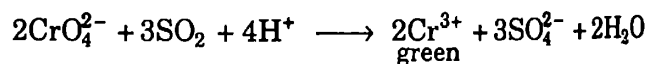
(d)  $\text{Ba}^{2+}$ :  $\text{K}_2\text{CrO}_4$  gives yellow precipitate of  $\text{BaCrO}_4$  with  $\text{Ba}^{2+}$  salts in presence of  $\text{CH}_3\text{COOH}$



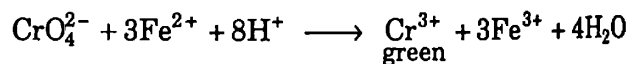
(e)  $\text{H}_2\text{S}$ :  $\text{H}_2\text{S}$  reduces acidified chromate solution to green chromium(III) ion accompanied by the separation of sulphur.



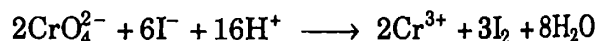
(f)  $\text{SO}_3^{2-}$ :  $\text{SO}_3^{2-}/\text{H}^+$  or  $\text{SO}_2$  reduces  $\text{CrO}_4^{2-}$  to  $\text{Cr}^{3+}$  (green)



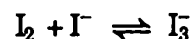
(f)  $\text{Fe}^{2+}$ :  $\text{Fe}^{2+}$  in presence of mineral acids reduces chromates to  $\text{Cr}^{3+}$  (green)



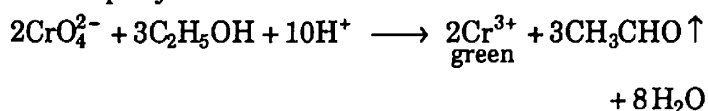
(g)  $\text{I}^-$  (**Iodides**): Iodide (KI) reduces  $\text{CrO}_4^{2-}$  to  $\text{Cr}^{3+}$  (green), and itself oxidised to  $\text{I}_2$



$\text{I}_2$  goes into solution as  $\text{I}_3^-$  (deep brown or bluish brown)



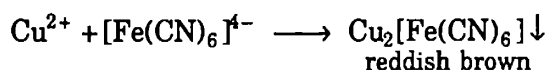
(h)  $\text{C}_2\text{H}_5\text{OH}$  : Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) in presence of mineral acid reduces chromates (or dichromates) slowly in cold but rapidly if the solution is heated



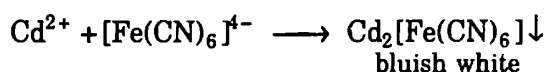
Smell of acetaldehyde ( $\text{CH}_3\text{CHO}$ ) is observed on heating the mixture.

(4)  $\text{K}_4[\text{Fe}(\text{CN})_6]$  Potassium hexacyanoferrate(II) (Potassium ferrocyanide)

(a)  $\text{Cu}^{2+}$  :  $\text{Cu}^{2+}$  salts on reaction with  $\text{CH}_3\text{COOH}$  and  $\text{K}_4[\text{Fe}(\text{CN})_6]$  give reddish brown precipitate of  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$

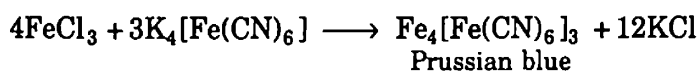


(b)  $\text{Cd}^{2+}$  :  $\text{Cd}^{2+}$  salts give bluish white precipitate of  $\text{Cd}_2[\text{Fe}(\text{CN})_6]$  under on reaction with  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and  $\text{CH}_3\text{COOH}$

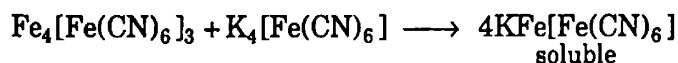


(c)  $\text{Zn}^{2+}$  : (Similar to  $\text{Cd}^{2+}$ )

(d)  $\text{Fe}^{3+}$  :  $\text{Fe}^{3+}$  salts forms blue coloured precipitate of  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  called **Prussian blue**



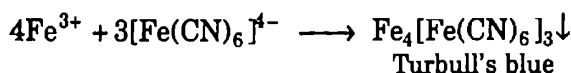
A large excess of the reagent dissolves Prussian blue partly or entirely when an intense blue colour is obtained.



(e)  $\text{Fe}^{2+}$  : When  $\text{K}_3[\text{Fe}(\text{CN})_6]$  is added to  $\text{Fe}^{2+}$  salts, first  $\text{K}_3[\text{Fe}(\text{CN})_6]$  oxidises  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and itself reduced to  $\text{K}_4[\text{Fe}(\text{CN})_6]$



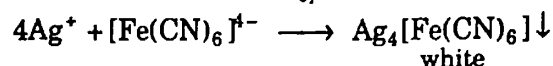
$\text{Fe}^{3+}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  combine to form a blue precipitate of **Turnbull's blue**



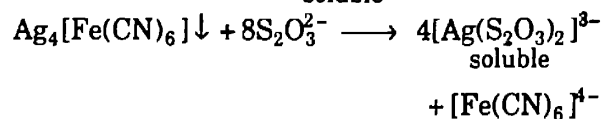
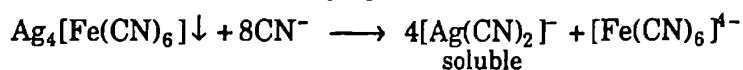
### DEEP Focus

We can observe that the composition of this precipitate is identical to that of Prussian blue. Earlier it was suggested that its composition was  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$  hence the different name. The identical composition and structure of Turnbull's blue and Prussian blue has recently been proved by **Mossbauer spectroscopy**. The precipitate is decomposed by  $\text{NaOH}$  or  $\text{KOH}$  forming  $\text{Fe}(\text{OH})_3$  — brown coloured precipitate.

(f)  $\text{Ag}^+$  : Silver salts ( $\text{AgNO}_3$ ) give white precipitate of  $\text{Ag}_4[\text{Fe}(\text{CN})_6]$  with  $\text{K}_4[\text{Fe}(\text{CN})_6]$



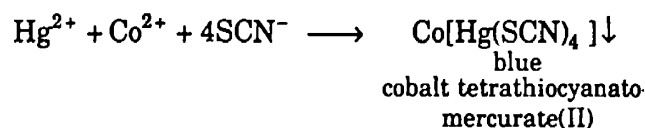
Precipitate dissolves in  $\text{KCN}$  and  $\text{Na}_2\text{S}_2\text{O}_3$  but remains insoluble in  $\text{NH}_3(\text{aq})$



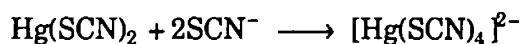
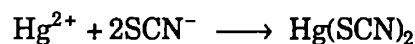
### 5. KSCN (Potassium thiocyanate solution)

**Note :** Instead  $\text{NH}_4\text{SCN}$  can also be used

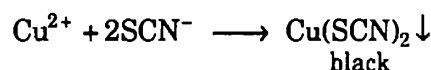
(a)  $\text{Hg}^{2+}$  (Mercuric ion) When  $\text{NH}_4\text{SCN}$  and cobalt acetate is added to  $\text{Hg}^{2+}$  solution, a blue colour precipitate is produced



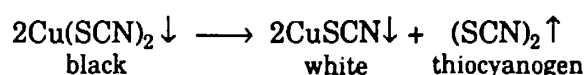
White precipitate of  $\text{Hg}(\text{SCN})_2$  readily soluble in excess of  $\text{NH}_4\text{SCN}$  is obtained



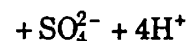
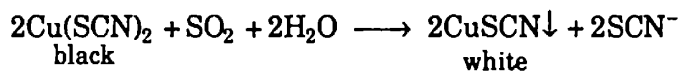
(b)  $\text{Cu}^{2+}$  :  $\text{NH}_4\text{SCN}$  on reaction with  $\text{Cu}^{2+}$  salts gives black precipitate of  $\text{Cu}(\text{SCN})_2$



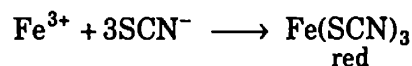
The precipitate decomposes slowly to form white precipitate of  $\text{CuSCN}$  along with thiocyanogen gas



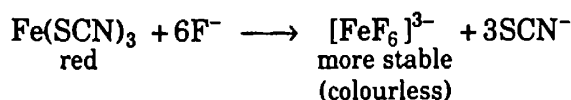
$\text{Cu}(\text{SCN})_2$  can be converted to  $\text{CuSCN}$  immediately by suitable reducing agent like  $\text{SO}_3^{2-}/\text{H}^+$



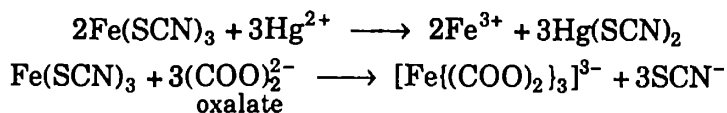
(c)  $\text{Fe}^{3+}$  :  $\text{NH}_4\text{SCN}$  reacts with  $\text{Fe}^{2+}$  salts in slightly acidic medium giving red colour solution of  $\text{Fe}(\text{SCN})_3$



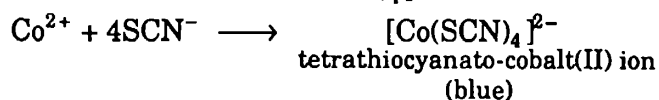
Sometime  $[\text{Fe}(\text{SCN})]^{2+}$  is also formed.  $\text{Fe}(\text{SCN})_3$  can be extracted by ether or amyl alcohol. Fluorides, oxalates and  $\text{Hg}(\text{II})$  ions bleach the red colour of  $\text{Fe}(\text{SCN})_3$ .





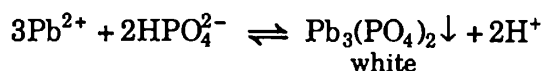


(d)  $\text{Co}^{2+}$ : On adding a few crystals of  $\text{NH}_4\text{SCN}$  to a neutral or acid solution of cobalt(II), a blue colour appears owing to the formation of  $[\text{Co}(\text{SCN})_4]^{2-}$



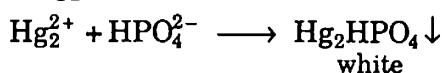
## 6. $\text{Na}_2\text{HPO}_4$

(a)  $\text{Pb}^{2+}$ :  $\text{Na}_2\text{HPO}_4$  gives white precipitate with  $\text{Pb}^{2+}$  salts

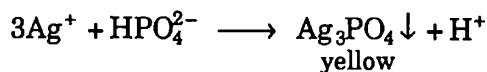


The reaction is reversible; strong acids ( $\text{HNO}_3$ ) dissolve the precipitate. The precipitate is also soluble in  $\text{NaOH}$ .

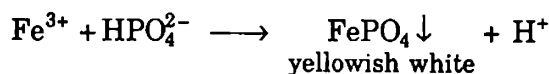
(b)  $\text{Hg}_2^{2+}$  (Mercurous):  $\text{Na}_2\text{HPO}_4$  gives white precipitate with  $\text{Hg}_2^{2+}$



(c)  $\text{Ag}^+$ :  $\text{Na}_2\text{HPO}_4$  in neutral solution gives yellow precipitate of silver phosphite with  $\text{Ag}^+$

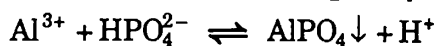


(d)  $\text{Fe}^{3+}$ :  $\text{NaH}_2\text{PO}_4$  gives yellowish-white precipitate with  $\text{Fe}^{3+}$  salts



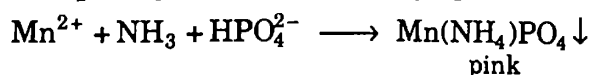
The reaction is reversible due to formation of strong acid ( $\text{H}^+$ ) which dissolves  $\text{FePO}_4$ . Hence,  $\text{FePO}_4$  is precipitated in presence of acidic buffer of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$ .

(e)  $\text{Al}^{3+}$ : White gelatinous precipitate of  $\text{AlPO}_4$  is obtained when  $\text{Al}^{3+}$  salts react with  $\text{Na}_2\text{HPO}_4$ .

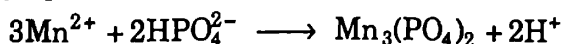


The reaction is reversible; strong acids dissolve the precipitate of  $\text{AlPO}_4$ . Precipitates are also soluble in  $\text{NaOH}$  but insoluble in  $\text{CH}_3\text{COOH}$ .

(f)  $\text{Mn}^{2+}$ :  $\text{Mn}^{2+}$  salts are precipitated as manganese ammonium phosphate,  $\text{Mn}(\text{NH}_4)\text{PO}_4 \cdot 7\text{H}_2\text{O}$ , (pink) on the addition of  $\text{Na}_2\text{HPO}_4$  in presence of  $\text{NH}_3(\text{aq})$

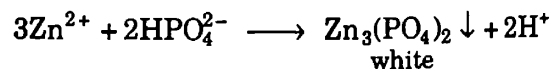


If  $\text{NH}_3(\text{aq})$  is absent,  $\text{Mn}_3(\text{PO}_4)_2$  is precipitated

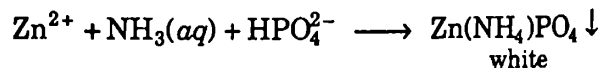


Both precipitates are soluble in acids.

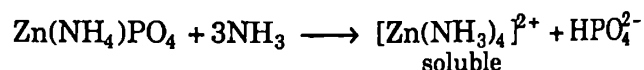
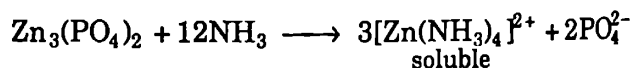
(g)  $\text{Zn}^{2+}$ :  $\text{Zn}^{2+}$  salts are precipitated as  $\text{Zn}_3(\text{PO}_4)_2$  on the addition of  $\text{Na}_2\text{HPO}_4$ .



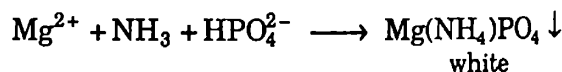
However, in presence of  $\text{NH}_3(\text{aq})$ ,  $\text{Zn}(\text{NH}_4)\text{PO}_4$  is precipitated



Both the precipitates are soluble in dilute acids. Excess of  $\text{NH}_3(\text{aq})$  dissolves the precipitates

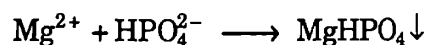


(h)  $\text{Mg}^{2+}$ :  $\text{Mg}^{2+}$  salts are precipitated as  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$  when  $\text{Na}_2\text{HPO}_4$  is added in presence of basic buffer ( $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ ).



The precipitate is sparingly soluble in water; soluble in acetic acid and in mineral acids. The precipitate separates slowly from dilute solutions because of its tendency to form supersaturated solutions; this may be overcome by cooling and by rubbing the test-tube with a glass rod.

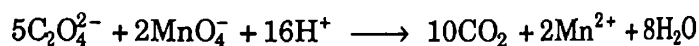
In neutral solution, a white flocculant precipitate of  $\text{MgHPO}_4$  is produced



## 7. $\text{MnO}_4^-$

All permanganates are soluble in water forming purple (reddish-violet) solutions

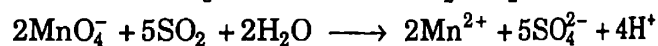
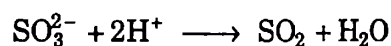
(a)  $\text{C}_2\text{O}_4^{2-}$  (Oxalate):  $\text{C}_2\text{O}_4^{2-}$  decolourises  $\text{KMnO}_4$  in acidic medium.



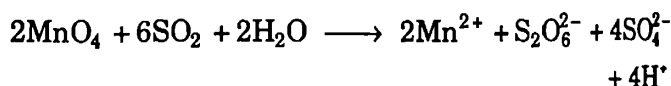
### DEEP Focus

The reaction is slow at room temperature but is rapid at  $60^\circ\text{C}$ . Manganese(II),  $\text{Mn}^{2+}$  ions, catalyse the reaction; thus reaction is autocatalytic; once  $\text{Mn}^{2+}$  ions are formed, it becomes faster.

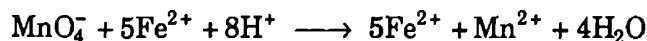
(b)  $\text{SO}_3^{2-}$ :  $\text{SO}_3^{2-}/\text{H}^+$  or  $\text{SO}_2$  also decolourises  $\text{MnO}_4^-$



Some dithionate ( $\text{S}_2\text{O}_6^{2-}$ ) may also be formed in this reaction, the quantity being dependent upon the experimental conditions:

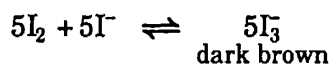
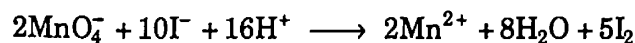


(c)  $\text{Fe}^{2+}$  :  $\text{Fe}^{2+}$  reduces  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$  and solution becomes yellow due to formation of  $\text{Fe}^{3+}$

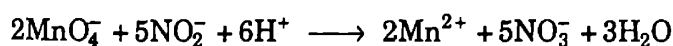


The yellow colour disappears if phosphoric acid or potassium fluoride is added due to formation of colourless complexes with  $\text{Fe}^{3+}$ .

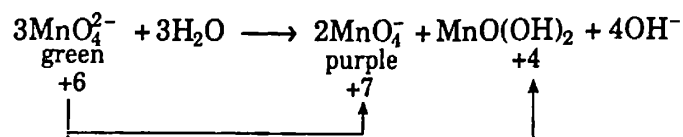
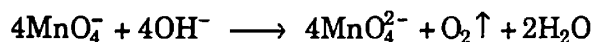
(d)  $\text{I}^-$  : KI reduces  $\text{MnO}_4^-/\text{H}^+$  and solution turn dark brown due to formation of  $\text{I}_3^-$



(e)  $\text{NO}_2^-$  :  $\text{NO}_2^-$  also decolourises  $\text{MnO}_4^-/\text{H}^+$



(f) Upon warming a concentrated solution of  $\text{KMnO}_4$  with concentrated  $\text{NaOH}$  solution, a green solution of  $\text{K}_2\text{MnO}_4$  (potassium manganate) is produced and  $\text{O}_2$  is evolved. When  $\text{K}_2\text{MnO}_4$  solution is diluted or acidified with dil.  $\text{H}_2\text{SO}_4$ , the purple colour of  $\text{KMnO}_4$  is restored and  $\text{MnO}_2$  (manganese dioxide) is precipitated (as  $\text{MnO}(\text{OH})_2$ ).

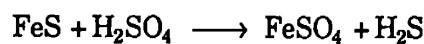


The  $\text{MnO}_4^{2-}$  disproportionates to  $\text{MnO}_4^-$  (oxidation) and  $\text{MnO}_2$  (reduction).

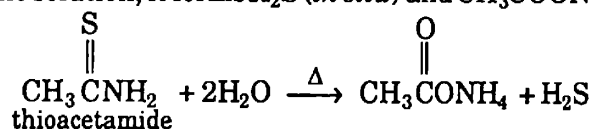
### 8. Thioacetamide

(Analysis of cations without  $\text{H}_2\text{S}$ )

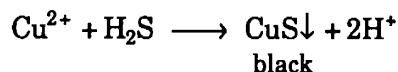
$\text{H}_2\text{S}$  in the laboratory is produced by reaction of  $\text{H}_2\text{SO}_4$  with  $\text{FeS}$



This causes lot of pollution and hence formation of  $\text{H}_2\text{S}$  by the above reaction should be discouraged. Thioacetamide serves as a source of  $\text{H}_2\text{S}$ . On hydrolysis in hot acidic solution, it forms  $\text{H}_2\text{S}$  (*in situ*) and  $\text{CH}_3\text{COONH}_4$ .



Thus, simply addition of thioacetamide in hot solution is the instant source of  $\text{H}_2\text{S}$  in the test-tube itself.

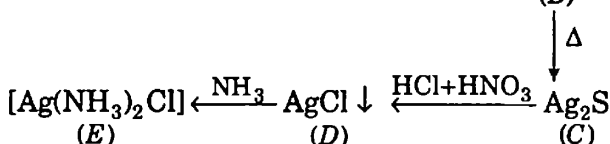
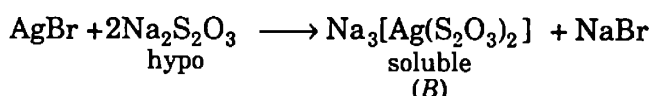


# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** (A) is yellow coloured solid partially soluble in aqueous  $\text{NH}_3$ . (A) is soluble in  $\text{Na}_2\text{S}_2\text{O}_3$  (hypo) solution forming a complex (B) which on heating is converted into (C) (black). (C) is converted into white ppt (D) on reaction with  $\text{HCl}$  and  $\text{HNO}_3$ . (D) is soluble in aqueous  $\text{NH}_3$  forming (E). Identify (A), (B), (C), (D) and (E) and explain reactions.

**Solution** (A) is  $\text{AgBr}$  (present in photographic plate)

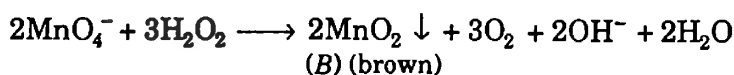
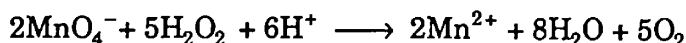


**Problem 2.** Identify (A) and (B) in the following and explain reactions given VD of (A) is 17.

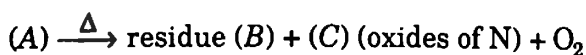
(A) decolourises acidified  $\text{KMnO}_4$ . (A) also gives brown ppt (B) with alkaline  $\text{KMnO}_4$ . (A) also liberates  $\text{I}_2$  from acidified  $\text{KI}$  solution. (A) also removes black stains from old oil paintings.

**Solution** Molecular weight of (A) =  $2 \times \text{VD}$  =  $34 \text{ g mol}^{-1}$ . Also (A) removes stains from old oil paintings.

$\Rightarrow$  (A) is  $\text{H}_2\text{O}_2$  (mol. wt. = 34)



**Problem 3.** (A) + tap water  $\longrightarrow$  white turbidity soluble in  $\text{aq NH}_3$



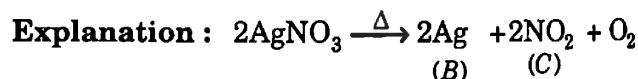
aqueous (A) gives brown ring on adding  $\text{FeSO}_4$  and conc.  $\text{H}_2\text{SO}_4$ . (C) is paramagnetic and forms dimer of VD 46. Identify (A), (B) and (C) and explain reactions.

**Solution** (A) + tap water  $\longrightarrow$  white turbidity soluble in  $\text{aq NH}_3$ . Tap water has  $\text{Cl}^-$  and turbidity is soluble in  $\text{aq NH}_3$ .

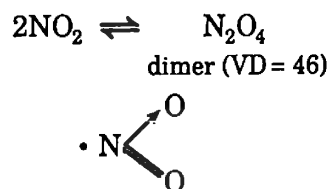
$\Rightarrow$  turbidity is of  $\text{AgCl}$  and thus (A) has  $\text{Ag}^+$

(A) also gives ring test of  $\text{NO}_3^-$

$\Rightarrow$  (A) has  $\text{NO}_3^-$  and thus (A) is  $\text{AgNO}_3$



$\text{NO}_2$  is paramagnetic due to one unpaired electron as shown and thus forms dimer by using unpaired electron.



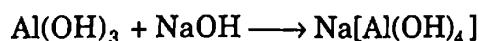
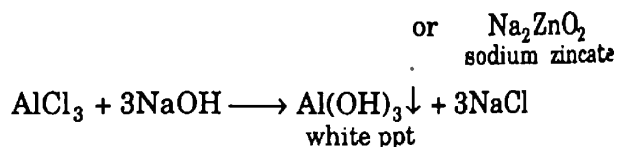
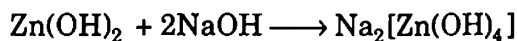
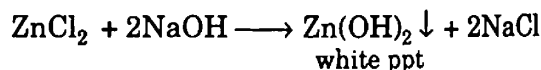
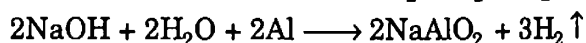
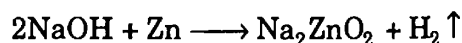
**Problem 4.** (A), an important laboratory reagent, turns red litmus blue, imparts golden yellow colour in flame and is a good precipitating agent. (A) reacts with  $\text{Zn}$  or  $\text{Al}$  forming  $\text{H}_2$  gas. (A) gives white ppt with  $\text{ZnCl}_2$  or  $\text{AlCl}_3$  but ppt dissolves in excess of (A). What is (A) and explain reactions?

**Solution** (A) turns blue litmus red  $\Rightarrow$  (A) is basic in nature.

(A) imparts golden yellow colour in flame  $\Rightarrow$  (A) has  $\text{Na}^+$ .

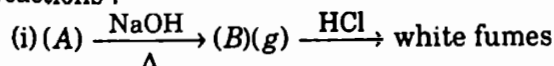
(A) gives  $\text{H}_2$  gas with  $\text{Zn}$  or  $\text{Al} \Rightarrow$  (A) is  $\text{NaOH}$ .

**Explanation :**

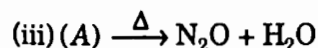


or  $\text{NaAlO}_2$   
sodium meta-aluminate

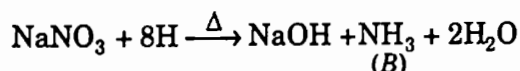
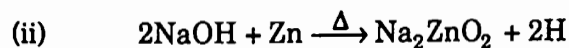
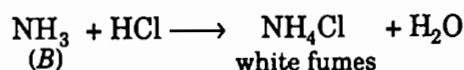
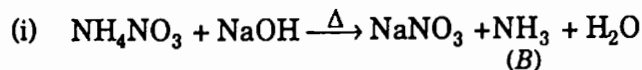
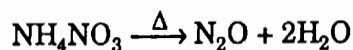
**Problem 5.** Identify (A) and (B) based on following reactions :



(ii) After (B) is expelled completely, resultant alkaline solution again gives gas (B) on heating with zinc.



**Solution** By (iii) (A) gives  $N_2O$ ,  $H_2O$  on heating, hence (A) is  $NH_4NO_3$



( $NH_3$  gas is obtained due to reduction of  $NO_3^-$ )

**Problem 6.** Identify (A), (B), (C) and (D) based on following observations :

(i) (A)  $\xrightarrow{\Delta}$  glassy transparent bead (B) on platinum wire

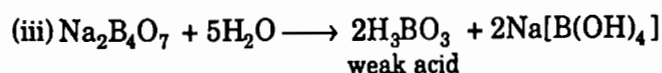
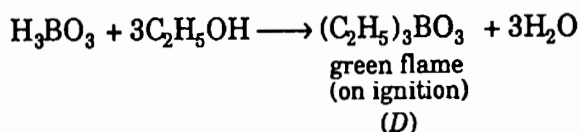
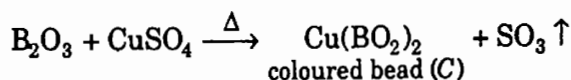
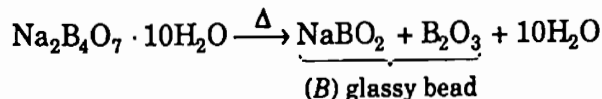
(B) +  $CuSO_4 \longrightarrow$  coloured bead (C)

(ii) (A) + conc.  $H_2SO_4$  +  $CH_3CH_2OH \xrightarrow{\text{ignite}}$  green flame (D)

(iii) Aqueous solution of (A) is alkaline.

**Solution** (i) (A) forms glassy transparent bead which is characteristic property of **borax**.

$\Rightarrow$  (A) is **borax** ( $Na_2B_4O_7 \cdot 10H_2O$ )



$Na[B(OH)_4]$  reacts with acid (HCl) hence aqueous solution of (A) is alkaline.

**Problem 7.** A colourless mixture of two salts (A) and (B) (excess) is soluble in  $H_2O$ . (A) turns blue litmus red and (B) turns red litmus blue. (A) gives white ppt with (B), which dissolves in excess of (B) forming (C). (A) when placed in atmosphere gives fumes and can form dimer. (A) gives white ppt with  $NH_4Cl$  and  $NH_4OH$  soluble in (B). Identify (A), (B) and (C) and explain reactions.

**Solution** (A) gives white ppt with  $NH_4Cl$  and  $NH_4OH$

$\Rightarrow$  (A) is  $Al^{3+}$

$\Rightarrow$  ppt is of  $Al(OH)_3$

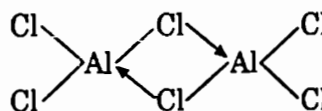
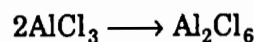
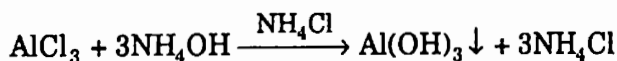
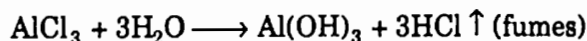
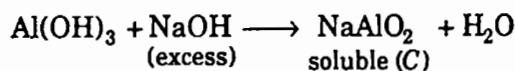
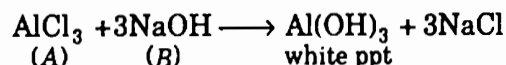
$Al(OH)_3$  is soluble in (B)  $\Rightarrow$  (B) is  $NaOH$

$\Rightarrow$  (C) is  $NaAlO_2$  (sodium meta-aluminate)

(A) forms dimer indicating (A) is electron-deficient that is the possible case of  $AlCl_3$ .

(A) is thus  $AlCl_3$  (acidic due to hydrolysis, turns blue litmus red)

(B) is  $NaOH$  (alkaline, turns red litmus blue)



**Problem 8.** Identify (A) based on following facts:

(a) (A) reduces  $HgCl_2$  solution to white ppt changing to grey.

(b) (A) turns  $FeCl_3$  yellow coloured solution to green.

(c) (A) gives white ppt with  $NaOH$  soluble in excess of  $NaOH$ .

(d) (A) gives yellow dirty ppt on passing  $H_2S$  gas, soluble in yellow ammonium sulphide (YAS).

(e) (A) gives chromyl chloride test.

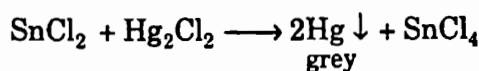
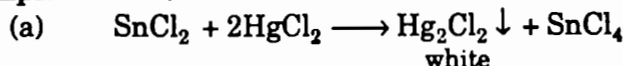
**Solution** (A) gives yellow dirty ppt with  $H_2S$  soluble in YAS

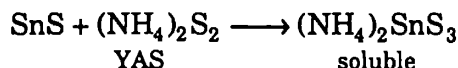
$\Rightarrow$  (A) has  $Sn^{2+}$

(A) gives chromyl chloride test (of  $Cl^-$ )

$\Rightarrow$  (A) has  $Cl^-$  ion and thus (A) is  $SnCl_2$

**Explanation :**



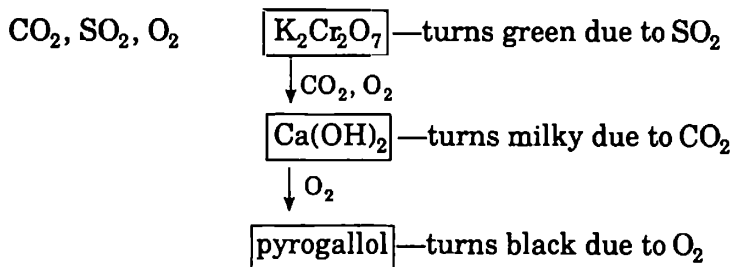


**Problem 9.** You have a mixture of CO<sub>2</sub>, SO<sub>2</sub> and O<sub>2</sub> gas. You have been provided following reagents for testing

- (a) lime water  
(b) acidified potassium dichromate solution  
(c) pyrogallol

Arrange these reagents in order such that only one gas is tested at one time.

**Solution** The correct order is (b), (a), (c)



**Note:** •  $\text{SO}_2$  and  $\text{CO}_2$  both turn lime water milky hence  $\text{Ca}(\text{OH})_2$  can't be used before  $\text{K}_2\text{Cr}_2\text{O}_7$ .

- $O_2$  is soluble in pyrogallol.

**Problem 10.** Identify gas (X) based on following facts:

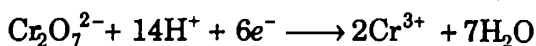
- (a) (X) occupies 0.35 L per g at NTP  
(b) (X) turns acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution green.  
(c) (X) decolourises acidified  $\text{KMnO}_4$  solution.  
(d) (X) gives white turbidity when  $\text{H}_2\text{S}$  gas is passed into

its aqueous solution.

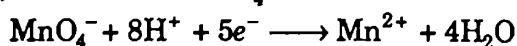
**Solution** (a) (X) occupies 0.35 L per g at NTP

$\Rightarrow$  molecular weight of (X) is  $64 \text{ g mol}^{-1}$

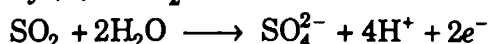
(b) (X) turns  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$  green, (X) is a reducing agent and green colour is due to formation of  $\text{Cr}^{3+}$ .



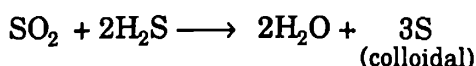
(c) (X) also reduces  $\text{MnO}_4^-/\text{H}^+$



$\Rightarrow$  probably (X) is  $\text{SO}_2$ .



(d)  $\text{SO}_2$  in aqueous solution gives white turbidity due to formation of colloidal sulphur.



**Problem 11.** (A) is a colourless salt with divalent cation. (A) gives yellow ppt with  $\text{K}_2\text{CrO}_4$  as well as with  $\text{AgNO}_3$ . (A) gives apple green colour in flame. (A) is precipitated by  $\text{H}_2\text{S}$  neither in acidic nor ammoniacal medium, but addition of  $(\text{NH}_4)_2\text{CO}_3$  in  $\text{NH}_4\text{OH}$  gave white ppt (B). 0.297 g of (A) gave 0.197 g of (B). Identify (A) and explain reactions.

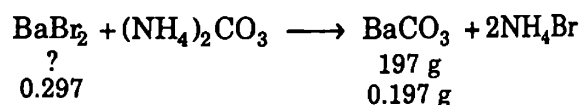
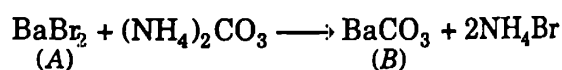
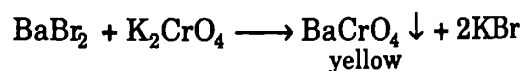
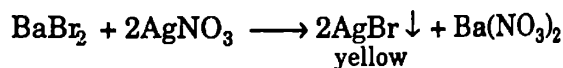
**Solution** (A) gives yellow ppt with KI as well as with  $\text{AgNO}_3$ .

⇒ (A) can have  $\text{Pb}^{2+}$  or  $\text{Ba}^{2+}$  (both divalent cations) and  $\text{Br}^-$ . (A) is not precipitated by  $\text{H}_2\text{S}$  in acidic and ammoniacal medium.

$\Rightarrow$  (A) does not have  $\text{Pb}^{2+}$  (precipitated as  $\text{PbS}$  in acidic medium by  $\text{H}_2\text{S}$  gas)

$\Rightarrow$  (A) contains  $\text{Ba}^{2+}$  (apple green flame)

$\Rightarrow$  (A) is **BaBr<sub>2</sub>**



$$\frac{M}{0.297} = \frac{197}{0.197}$$

•

$$M(\text{BaBr}_2) = 297 \text{ g mol}^{-1}$$

Thus, A is  $\text{BaBr}_2$

(Ba = 137, Br = 80).

**Problem 12.** A colourless salt (A), soluble in water, gives a mixture of three gases (B), (C) and (D) along with water vapours. (B) is blue, (C) is red and gas (D) is neutral towards litmus paper. Gas (B) is also obtained when (A) is heated with NaOH and gives brown ppt with  $\text{K}_2\text{HgI}_4$ . Solution thus obtained gives white ppt (E) with  $\text{CaCl}_2$  solution in presence of  $\text{CH}_3\text{COOH}$ . (E) decolorises  $\text{MnO}_4^-/\text{H}^+$ . Gas (C) turns lime water milky while gas (D) burns with blue flame and is fatal when inhaled.

Identify (A) to (D) and explain reactions.

**Solution** Gas (B) gives brown ppt with  $K_2HgI_4$

$\Rightarrow$  gas (B) is **NH<sub>3</sub>**

$\Rightarrow$  (A) has  $\text{NH}_4^+$

**Gas (C) turns lime water milky**

$\Rightarrow$  gas (C) can be  $\text{SO}_2$  or  $\text{CO}_2$

Gas (D) is also obtained along with (C). Gas (D) burns with blue flame and is fatal when inhaled

$\Rightarrow$  gas ( $D$ ) is **CO**

$\Rightarrow$  gas (C) is **CO<sub>2</sub>**

$\Rightarrow (A)$  has  $\text{C}_2\text{O}_4^{2-}$  ion

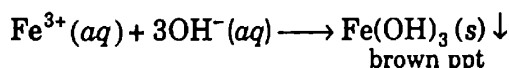
$$\text{AgCl} + 2\text{NH}_3(aq) \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$$

soluble

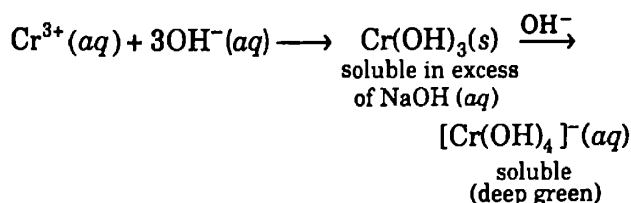
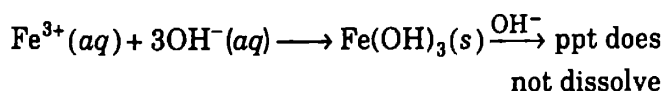


**Solution** (a)  $\text{Fe}^{3+}$  and  $\text{Na}^+$ :

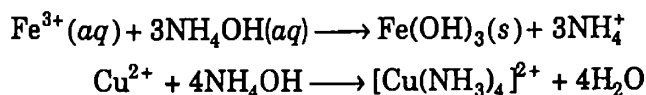
Add excess of aq KOH.  $\text{Fe}^{3+}$  is precipitated as  $\text{Fe}(\text{OH})_3$ .  $\text{Na}^+(\text{aq})$  remains in solution.

(b)  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$ :

Add excess of aq NaOH.  $\text{Fe}^{3+}$  is precipitated as  $\text{Fe}(\text{OH})_3$  while  $\text{Cr}(\text{OH})_3$  first formed dissolves in excess of aq NaOH.

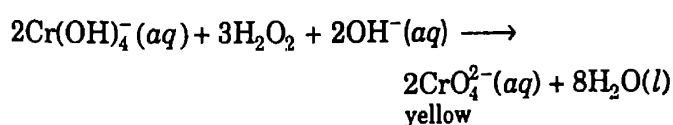
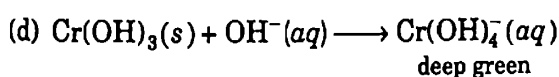
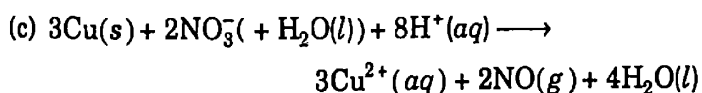
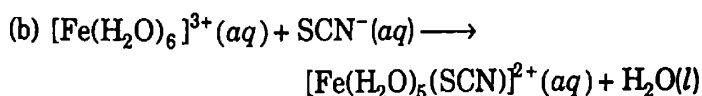
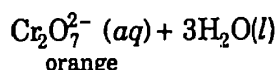
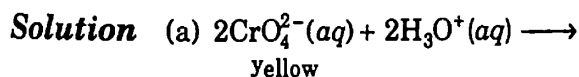
(c)  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$ :

Add excess of aq  $\text{NH}_3(\text{NH}_4\text{OH})$ .  $\text{Fe}^{3+}$  is precipitated as  $\text{Fe}(\text{OH})_3$  while  $\text{Cu}^{2+}$  forms deep blue coloured soluble complex  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ .

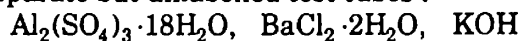


**Problem 20.** Write a balanced net ionic equation for each of the following reactions:

- A  $\text{CrO}_4^{2-}$  solution turns from yellow to orange upon addition of acid.
- $\text{Fe}^{3+}(\text{aq})$  reacts with  $\text{KSCN}(\text{aq})$  to give deep red solution.
- Copper metal reacts with nitric acid to give NO gas and a blue solution.
- A deep green solution of  $\text{Cr}(\text{OH})_3$  in excess base turns yellow on addition of hydrogen peroxide.



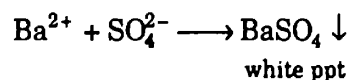
**Problem 21.** The following solid substances are in separate but unlabelled test tubes:



Describe how could you identify the compounds by chemical tests using only these substances and water?

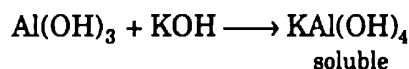
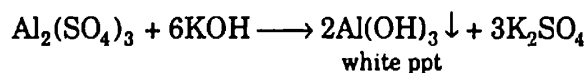
**Solution** All the above substances are unlabelled. Label the test-tubes I, II and III.

Mix I and II in aqueous solution. If there is formation of white ppt, then these are  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  and  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$



III is certainly KOH.

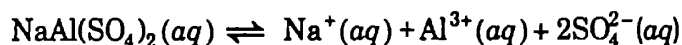
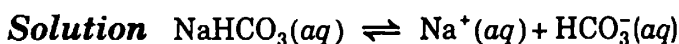
- Add III into I, if there is white ppt and ppt dissolves in excess of III then I is  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$



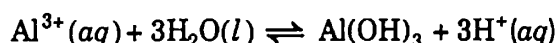
- Add III into II and there is no ppt formation then II is certainly  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  thus

I is  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , II is  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and III is KOH.

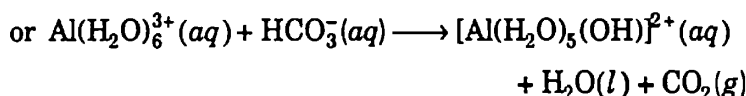
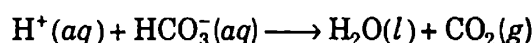
**Problem 22.** Baking powders contain sodium (or potassium) hydrogen carbonate and an acidic substance. When water is added to a baking powder, carbon dioxide is released. One kind of baking powder contains  $\text{NaHCO}_3$  and sodium aluminium sulphate,  $\text{NaAl}(\text{SO}_4)_2$ . Write the net ionic equation for the reaction that occurs in water solution.



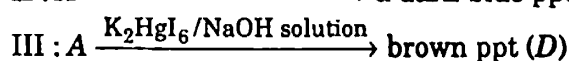
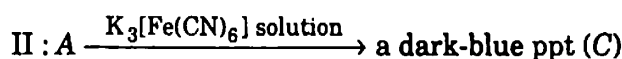
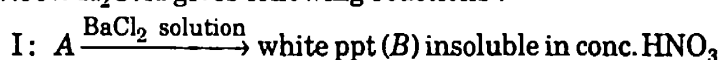
$\text{Al}^{3+}$  solution is acidic due to hydrolysis



$\text{H}^+(\text{aq})$  decomposes  $\text{HCO}_3^-(\text{aq})$  forming  $\text{CO}_2(\text{g})$



**Problem 23.** A light coloured crystalline solid A has 27.55%  $\text{H}_2\text{O}$ . A gives following reactions:



Identify A



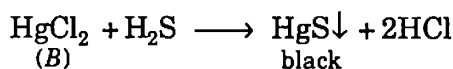
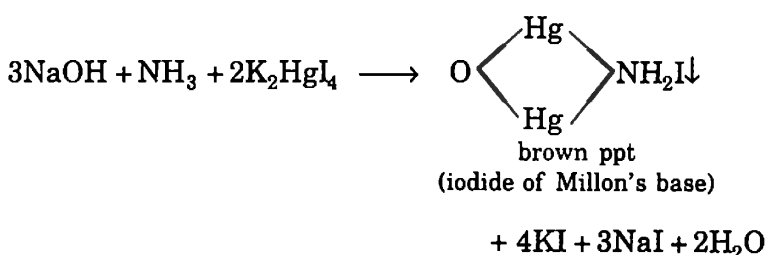
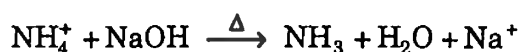
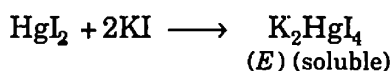
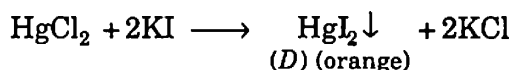
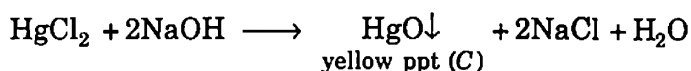
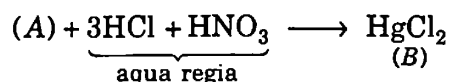




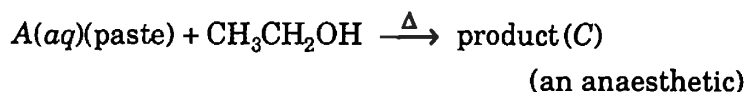
**Solution** (A) is insoluble in dil.  $\text{HNO}_3$ .

$\Rightarrow$  (A) is of group II (copper subgroup) and is  $\text{HgS}$  [only]

$\text{HgS}$  (black) is insoluble in dil.  $\text{HNO}_3$



**Problem 31.** Identify (A) to (C) in the following :



**Solution**  $\text{CH}_3\text{CH}_2\text{OH} + A(aq)(\text{paste}) \longrightarrow \text{product (C)}$

(C) is an anaesthetic from  $\text{CH}_3\text{CH}_2\text{OH}$

$\Rightarrow$  (C) is  $\text{CHCl}_3$

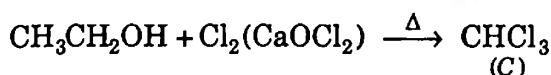
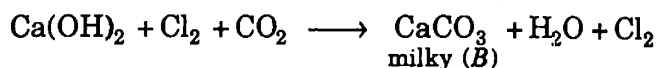
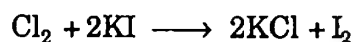
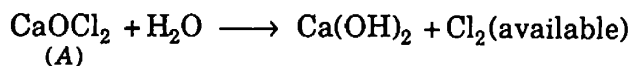
$\Rightarrow$  (A) contains Cl

(A) with  $\text{CO}_2$  gives milkiness

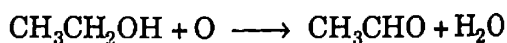
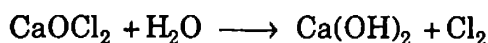
$\Rightarrow$  (A) contains  $\text{Ca(OH)}_2$  in aqueous solution.

(A) is  $\text{CaOCl}_2$  (bleaching powder)

**Explanation :**



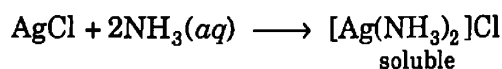
Formation of C is explained by following reactions :



**Problem 32.** Aqueous solution of (A) is deep yellow but (A) (solid) is brown. (A) aqueous solution gives white ppt with  $\text{AgNO}_3$  soluble in  $\text{NH}_3$ . Yellow solution of (A) changes to green solution (B) on passing  $\text{H}_2\text{S}$ . (A) is precipitated as brown ppt (C) on adding  $\text{NH}_4\text{OH}$  in presence of  $\text{NH}_4\text{Cl}$ . Precipitate (C) is insoluble in  $\text{NaOH}$  even in presence of oxidising agents but (C) dissolves in  $\text{HCl}$  forming (A) again. Aqueous (A) gives blue colouration (D) with  $\text{K}_4[\text{Fe(CN)}_6]$ . Aqueous (B) also gives blue colouration (E) with  $\text{K}_3[\text{Fe(CN)}_6]$ . Identify (A) to (E) and explain difference between (D) and (E).

**Solution** A gives white ppt with  $\text{AgNO}_3$  soluble in  $\text{NH}_3$ .

$\Rightarrow$  (A) has  $\text{Cl}^-$

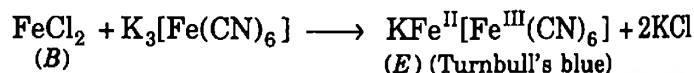
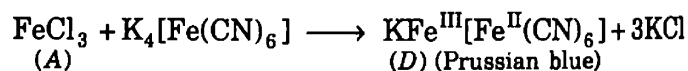
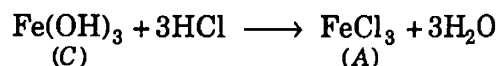
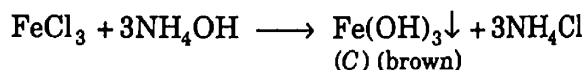
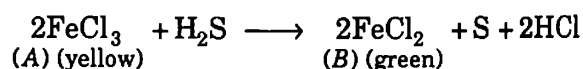


(A) is precipitated as brown ppt. (C) by  $\text{NH}_4\text{OH}$  in presence of  $\text{NH}_4\text{Cl}$

$\Rightarrow$  (A) has  $\text{Fe}^{3+}$  (of III group) which is confirmed by formation of blue colouration with  $\text{K}_4[\text{Fe(CN)}_6]$

$\Rightarrow$  (A) is  $\text{FeCl}_3$

**Explanation :**



## DEEP Focus

X-ray studies have established that Prussian blue and Turnbull's blue are identical. In (D),  $\text{Fe}^{3+}$  partially oxidises  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$  forming some  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$  and in (E),  $\text{Fe}^{2+}$  partially reduces  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$  forming some  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ . Thus, both (D) and (E) have  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$  and  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ .

**Problem 33.** (A) is scarlet (reddish-orange) inorganic salt insoluble in  $H_2O$ . (A) on reaction with  $HNO_3$  gives blackish-brown residue (B) and colourless solution of (C). (C) gives yellow ppt with KI solution as well as with  $K_2CrO_4$ . (C) also gives black ppt (D) with  $H_2S$  in HCl solution, ppt (D) dissolves in dil.  $HNO_3$ . (B) on heating with conc.  $HNO_3$  and  $Mn(NO_3)_2$  forms pink coloured solution (E). Identify (A), (B), (C), (D) and (E).

**Solution** (C) is colourless soluble solution.

(C) give black ppt with  $H_2S/HCl$

$\Rightarrow$  (C) is of group II

(C) gives yellow ppt with KI as well as with  $K_2CrO_4$

$\Rightarrow$  (C) has  $Pb^{2+}$  ion

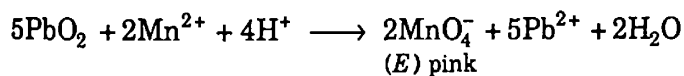
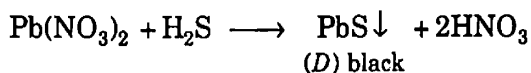
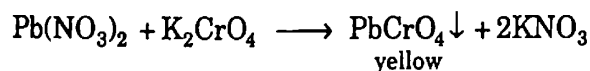
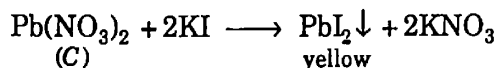
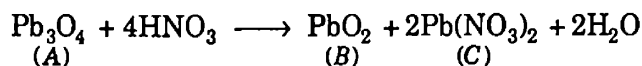
Thus, (C) is  $Pb(NO_3)_2$  obtained from (A), (B) on heating with  $Mn^{2+}$  and  $HNO_3$  gives purple colour which is due to oxidation of  $Mn^{2+}$  of  $HMnO_4$  (purple)

$\Rightarrow$  (B) is oxidising agent

$\Rightarrow$  (B) is  $PbO_2$  (blackish-brown)

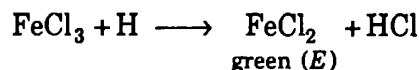
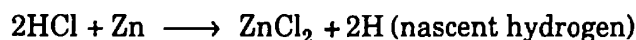
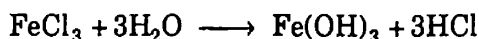
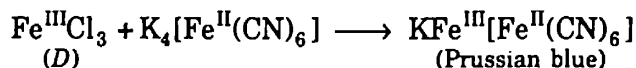
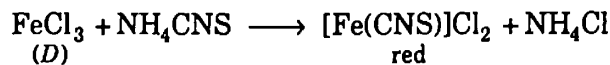
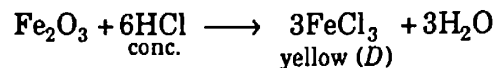
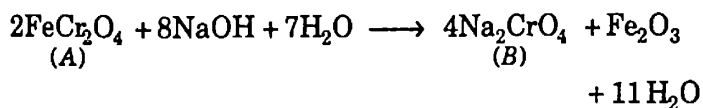
$\Rightarrow$  (A) is double oxide of lead.

(A) is  $Pb_3O_4$  (red lead) ( $2PbO \cdot PbO_2$ )



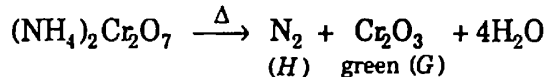
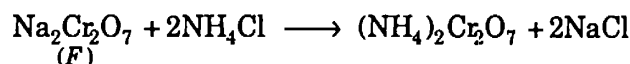
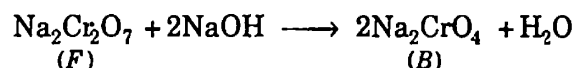
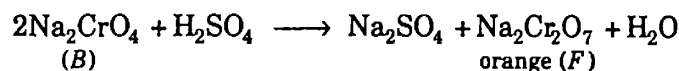
**Problem 34.** Chromite ore (A) ( $FeCr_2O_4$ ) is fused with NaOH in presence of  $H_2O_2$  when yellow coloured solution (B) and residue (C) are obtained. (C) is separated by filtration and dissolved in conc. HCl forming a yellow coloured solution (D). (D) gives red colour with  $NH_4CNS$  and blue colour with  $K_4[Fe(CN)_6]$ . (D) changes to green (E) when Zn is added into it, however,  $H_2$  gas if passed into (D) has no effect. (B) changes to orange (F) on reaction with dil.  $H_2SO_4$  and again (F) changes to (B) on adding NaOH. (F) on reaction with  $NH_4Cl$  and subsequent heating gives G (green) and H (gas). Identify (B) to (H) and explain reactions.

**Solution**  $A(FeCr_2O_4)$  is an ore of chromium.



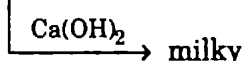
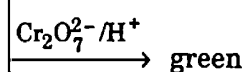
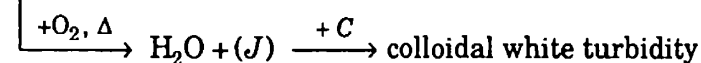
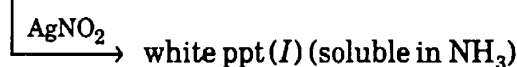
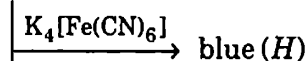
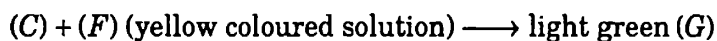
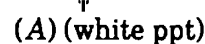
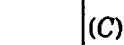
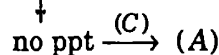
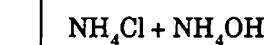
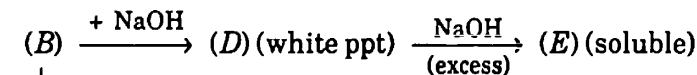
### DEEP Focus

[Nascent hydrogen is more reactive than molecular  $H_2$  hence  $H_2$  gas passed into  $FeCl_3$  solution has no effect.  $FeCl_3$  solution is acidic due to hydrolysis, hence Zn added into it gives nascent hydrogen (in situ) that causes reduction of  $FeCl_3$  into  $FeCl_2$ ]



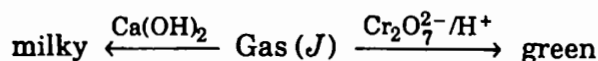
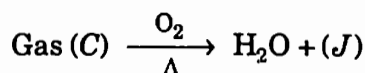
**Note :** ( $Cr_2O_3$  can be reduced to Cr by Al.)

**Problem 35.** Colourless salt, (A) (insoluble in water) + dil.  $H_2SO_4 \longrightarrow (B) + C(g)$



Identify (A) to (J) and explain reactions.

**Solution** Gas (C) is vital compound in this scheme.



$\Rightarrow (\text{J})$  is  $\text{SO}_2$

$\Rightarrow (\text{C})$  is  $\text{H}_2\text{S}$  (giving  $\text{H}_2\text{O}$  and  $\text{SO}_2$  by combustion in  $\text{O}_2$ ).

(B) gives white ppt only if (C) is passed into its ammoniacal solution containing  $\text{NH}_4\text{Cl}(\text{NH}_4\text{OH} + \text{NH}_4\text{Cl})$

$\Rightarrow (\text{B})$  has  $\text{Zn}^{2+}$  and (B) is  $\text{ZnSO}_4$

$\Rightarrow (\text{A})$  has  $\text{Zn}^{2+}$  ion

$\Rightarrow (\text{A})$  is  $\text{ZnS}$

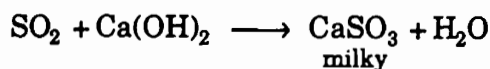
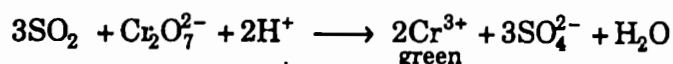
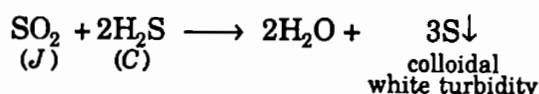
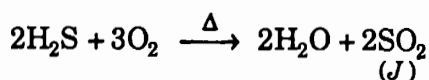
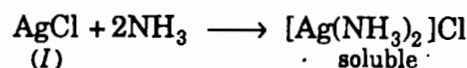
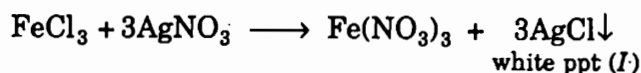
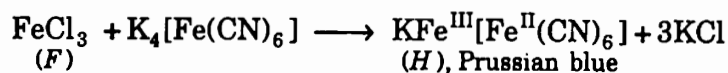
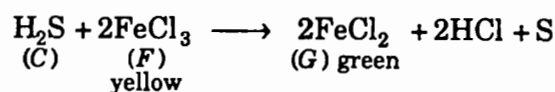
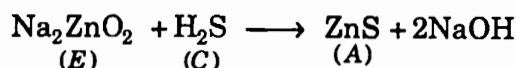
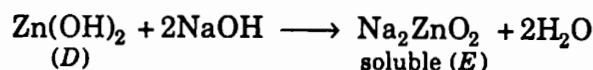
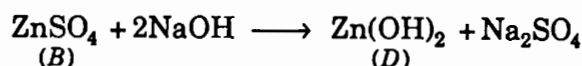
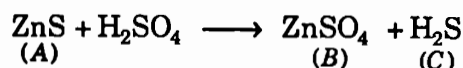
(F) gives blue colour with  $\text{K}_4[\text{Fe}(\text{CN})_6]$

$\Rightarrow (\text{F})$  has  $\text{Fe}^{3+}$  ion

(F) gives white ppt with  $\text{AgNO}_3$

$\Rightarrow (\text{F})$  has  $\text{Cl}^-$  ion. Thus, F is  $\text{FeCl}_3$ .

**Explanation :**

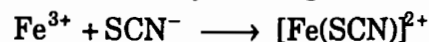


**Problem 36.** A solution may contain any of the following ions :  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ . Based on the following experiment and results therein, indicate which of the ions would be present? Indicate any wrong information, if any.

- The original solution is treated with  $(\text{NH}_4)_2\text{S}$  (a substitute of  $\text{H}_2\text{S}$ ) in a buffered basic solution. A dark precipitate is obtained.
- The ppt for (a) dissolves in aqua-regia
- The filtrate after separating ppt in (a) is treated with  $\text{NaOH}$  and  $\text{H}_2\text{O}_2$ . A dark ppt is separated. Filtrate is colourless.
- The ppt from (c) dissolves in  $\text{HCl}$  (aq) giving a coloured solution.
- The solution from (d) is treated with aqueous  $\text{NH}_3$ . A dark ppt forms.
- The ppt from (e) is soluble in  $\text{HCl}$  (aq) and solution develops an intense red colour when treated with  $\text{SCN}^-$  (aq).

**Solution**

- Precipitate can be of  $\text{NiS}$
- $\text{NiS}$  dissolves in aqua regia
- Precipitate can be of  $\text{Fe(OH)}_3$
- $\text{Fe(OH)}_3$  is soluble in  $\text{HCl}$  (aq) giving (yellow) coloured solution of  $\text{FeCl}_3$ .
- This step is incorrect since filtrate of step (c) is already colourless indicating absence of  $\text{Cr}^{3+}$ .
- This confirms  $\text{Fe}^{3+}$  by forming intense red colour



Thus,  $\text{Fe}^{3+}$  — confirmed

$\text{Ni}^{2+}$  — probable

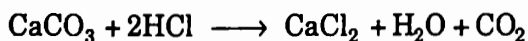
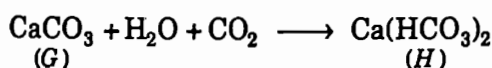
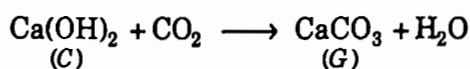
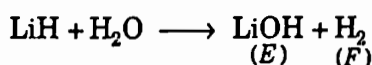
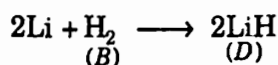
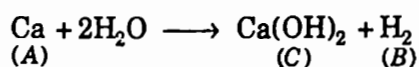
$\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$  — absent

**Problem 37.** On treatment with cold water, an element (A) reacted quietly, liberating a colourless, odourless gas (B), and a solution (C). Lithium reacted with (B) yielding a solid product (D) which effervesced with water to give a strongly basic solution (E) and gas (F). When  $\text{CO}_2$  was bubbled through solution (C) and initial white ppt (G) was formed, but this re-dissolved, forming solution (H) when more  $\text{CO}_2$  was added. ppt (G) effervesced when moistened with conc.  $\text{HCl}$ , and gave a deep brick red colouration to a Bunsen burner flame. When (G) was heated with carbon at  $1000^\circ\text{C}$  a caustic white compound (I) was formed, which when heated with  $\text{N}_2$  at  $1000^\circ\text{C}$  gave a solid (J) of some commercial importance. Name the compounds (A) to (J) and explain reactions.

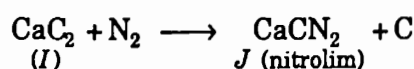
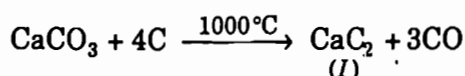
**Solution** When  $\text{CO}_2$  is passed into (C), white ppt (G) was formed which re-dissolved in excess of  $\text{CO}_2$

$\Rightarrow (\text{C})$  is  $\text{Ca(OH)}_2$

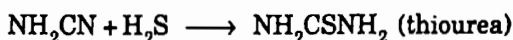
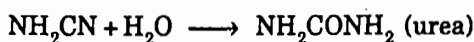
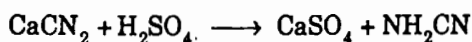
$\Rightarrow (\text{A})$  is  $\text{Ca}$

**Explanation :**

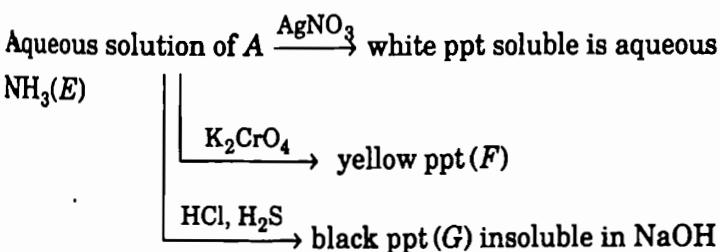
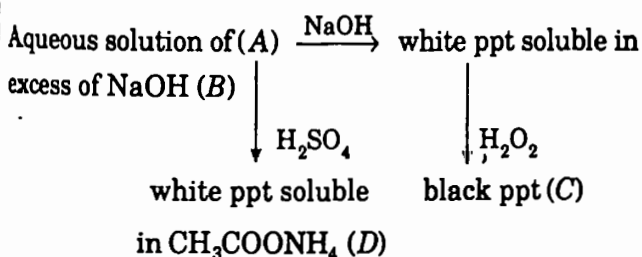
Brick red colour in flame is due to  $\text{CaCl}_2$

**DEEP Focus**

$\text{CaCN}_2$  is of industrial importance. It is used to make urea, thiourea etc.

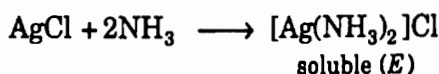
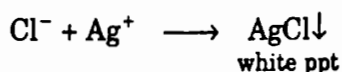


**Problem 38.** Identify colourless salt (A) based on the following reactions :



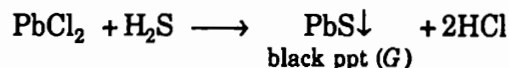
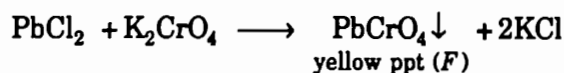
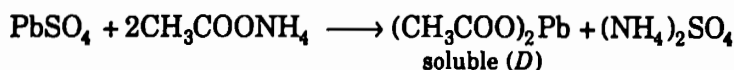
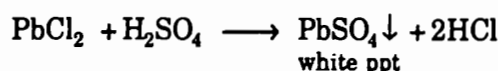
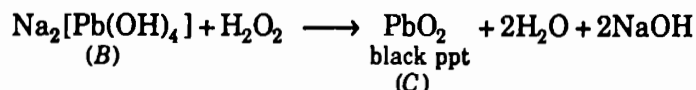
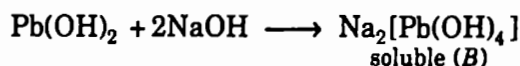
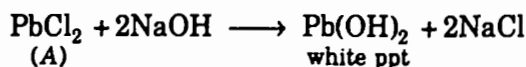
**Solution** A  $\xrightarrow{\text{AgNO}_3}$  white ppt soluble in aq  $\text{NH}_3$

Thus, A contains  $\text{Cl}^-$  as anion.



Thus, A (colourless salt) can contain  $\text{Hg}^{2+}$  or  $\text{Pb}^{2+}$  or  $\text{Bi}^{3+}$  as cation.

Since, A gives yellow ppt with  $\text{K}_2\text{CrO}_4$ , hence A contains  $\text{Pb}^{2+}$  as cation. Thus, A is  $\text{PbCl}_2$ .

**Reactions :**

**Problem 39.** Identify (A) to (F) based on the following reactions:

Brownish black oxide (A) + dil.  $\text{HCl} \longrightarrow$  green coloured solution (B) + gas (C)

(B) + aq  $\text{NH}_3$  +  $\text{H}_2\text{S}$  gas  $\longrightarrow$  black ppt (D)

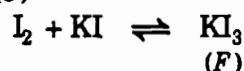
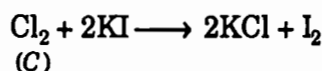
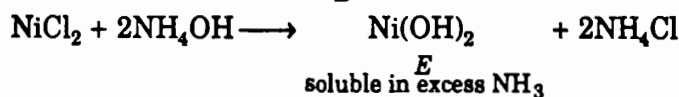
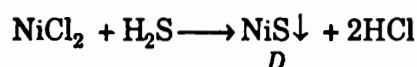
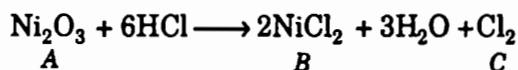
(B) + aq  $\text{NH}_3 \longrightarrow$  green ppt (E) soluble in excess of aq  $\text{NH}_3$

(C) + aq  $\text{KI} \longrightarrow$  reddish brown solution (F)

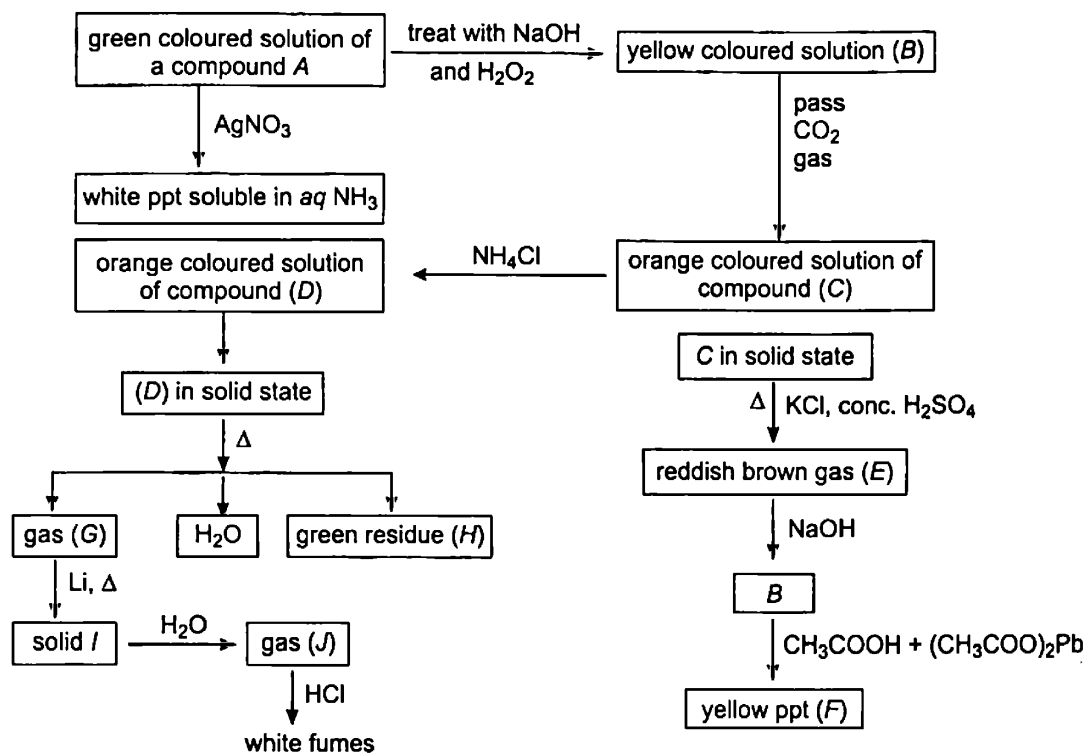
**Solution** Ammoniacal solution of B (green) gives black ppt with  $\text{H}_2\text{S}$  hence (B) has  $\text{Ni}^{2+}$  ion and exists as  $\text{NiCl}_2$  due to dissolution of (A) in dil  $\text{HCl}$ .

(A) also contains nickel ion but in +3 oxidation state which is reduced +2 by dil  $\text{HCl}$

Thus, A is  $\text{Ni}_2\text{O}_3$

**Reactions :**

**Problem 40.** Identify (A) to (J) based on following observations :



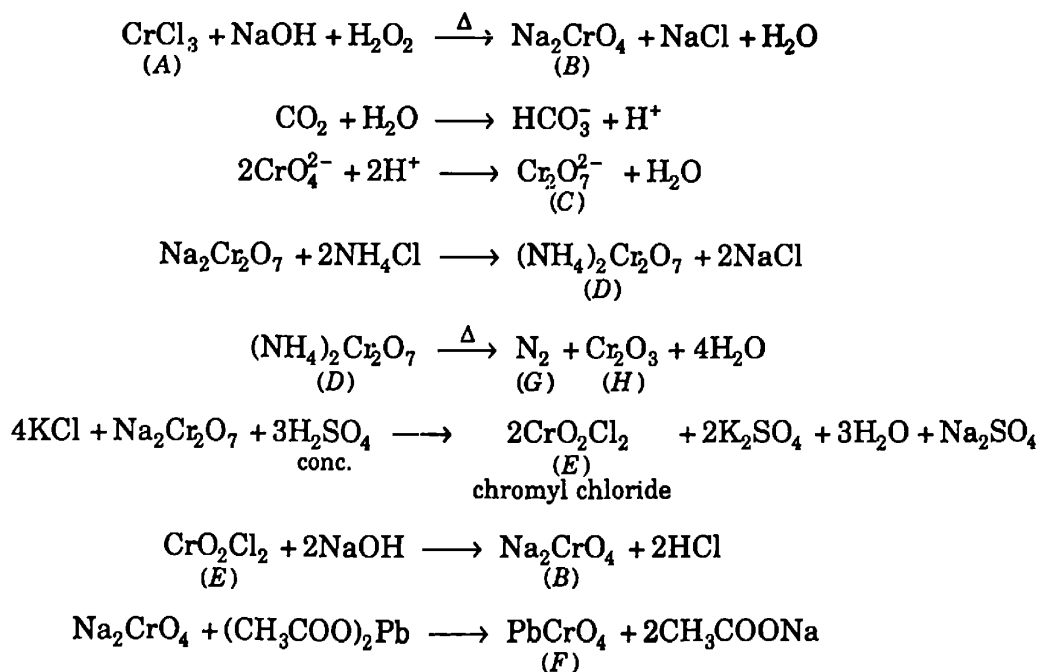
### Solution

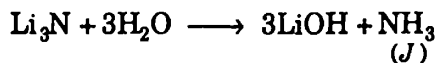
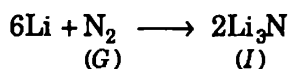
| Observations                                                                                                  | Inference                                                                    |
|---------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------|
| A gives white ppt. soluble in aq. $\text{NH}_3$ , with $\text{AgNO}_3$                                        | A contains $\text{Cl}^-$                                                     |
| $\text{C} + \text{conc. H}_2\text{SO}_4 + \text{KCl} \xrightarrow{\Delta} \xrightarrow{\text{NaOH}} \text{B}$ | This is chromyl-chloride test thus C is $\text{Na}_2\text{Cr}_2\text{O}_7$ . |
| $\text{B} + (\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}} \text{yellow ppt}$        | Thus, B is $\text{CrO}_4^{2-}$ ( $\text{Na}_2\text{CrO}_4$ ).                |

Other compounds are thus :

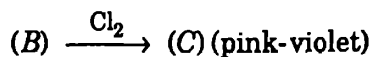
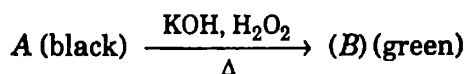
|                        |                                 |                                          |                                              |                                 |
|------------------------|---------------------------------|------------------------------------------|----------------------------------------------|---------------------------------|
| (A) : $\text{CrCl}_3$  | (B) : $\text{Na}_2\text{CrO}_4$ | (C) : $\text{Na}_2\text{Cr}_2\text{O}_7$ | (D) : $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ | (E) : $\text{CrO}_2\text{Cl}_2$ |
| (F) : $\text{PbCrO}_4$ | (G) : $\text{N}_2$              | (H) : $\text{Cr}_2\text{O}_3$            | (I) : $\text{Li}_3\text{N}$                  | (J) : $\text{NH}_3$             |

**Reactions** (unbalanced/poartial) :





**Problem 41.** Identify (A), (B) and (C) in the following scheme :



(C) is good laboratory reagent in acidic, basic and neutral medium.

(C) can be decolourised by  $\text{Fe}^{2+}$ ,  $\text{C}_2\text{O}_4^{2-}$  in acidic medium and by  $\text{C}_2\text{H}_4$  (ethene) in basic medium (in which brown ppt occurs)

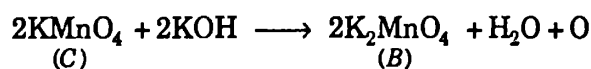
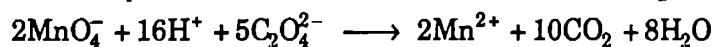
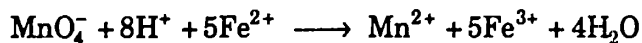
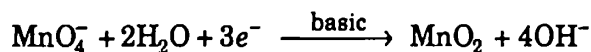
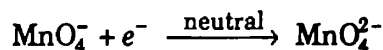
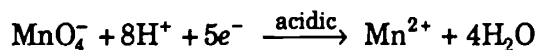
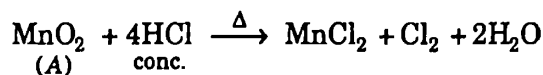
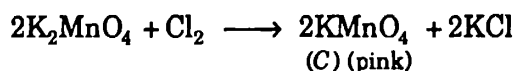
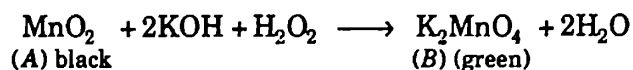


**Solution** Reactions indicate that (C) is  $\text{KMnO}_4$  and (A) is thus  $\text{MnO}_2$ .

$\text{KMnO}_4$  can oxidise  $\text{Fe}^{2+}$ ,  $\text{C}_2\text{O}_4^{2-}$  in acidic medium and used as reagent (Baeyer) in basic medium for testing unsaturation of alkenes and alkynes.

Thus, (A) is  $\text{MnO}_2$ .

**Explanation :**



(Also refer  $\text{KMnO}_4$  in chapter 16)



# Chapter Proficiency Exercises

## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

1.  $\text{BaCl}_2$  gives white precipitate with an aqueous solution of a salt. Identify acid radical.
2.  $\text{PO}_4^{3-}$  and  $\text{AsO}_4^{3-}$  can be identified by a reagent. Name the reagent. Write reaction.
3. A mixture contains,  $\text{CO}_3^{2-}$ ,  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$ . Give scheme to identify them.
4.  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  both give white ppt with  $\text{BaCl}_2$  solution. How is  $\text{SO}_3^{2-}$  detected in presence of  $\text{SO}_4^{2-}$ ?
5.  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} + \text{conc. H}_2\text{SO}_4 \xrightarrow{\Delta} (\text{A}) \xrightarrow{\text{CH}_3\text{OH}, \Delta} (\text{B})$ .  
Identify (A) and (B).
6.  $\text{SO}_4^{2-}$  also gives white ppt with lead acetate but ppt dissolves in ammonium acetate solution. Explain.

7. (A) +  $\text{KBr} \longrightarrow$  yellow ppt (B)

(A) + conc.  $\text{H}_2\text{SO}_4 \xrightarrow{\Delta}$  brown vapours intensified with Cu-turnings.

(B) dissolves in hypo forming a soluble complex (C). What are (A), (B) and (C) and explain their reactions?

8. (A) + dil.  $\text{H}_2\text{SO}_4 \xrightarrow{\Delta}$  gas (B). Gas (B) turns  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$  solution green.  
Aqueous solution of (A) +  $\text{BaCl}_2 \longrightarrow$  white ppt (C). Filtrate after removing (C) +  $\text{Br}_2$  water  $\longrightarrow$  white ppt (C). Identify (A), (B) and (C).

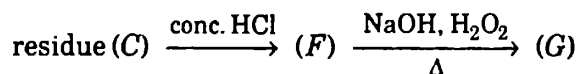
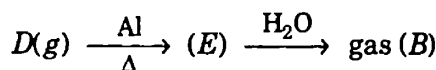
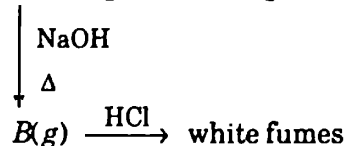
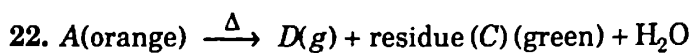
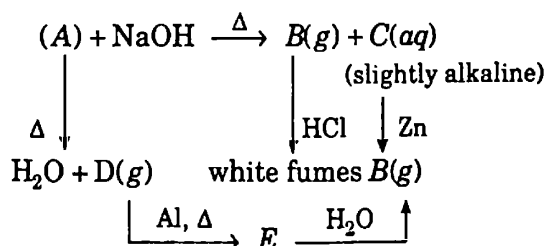
9. In the top space write the formula for each substance formed when the following ion pairs are mixed. Use the bottom space to describe any visible change, i.e., white precipitate formed, solution turns red, etc. If no visible change occurs, leave the space blank.

### Cations

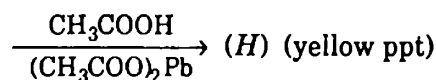
| Reagent added                             | $\text{Pb}^{2+}$ | $\text{Cu}^{2+}$ | $\text{Fe}^{3+}$ | $\text{Co}^{2+}$ | $\text{Zn}^{2+}$ | $\text{Mg}^{2+}$ | $\text{Ba}^{2+}$ | $\text{K}^+$ |
|-------------------------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|--------------|
| $(\text{NH}_4)_2\text{SO}_4$              | $\text{PbSO}_4$  |                  |                  |                  |                  |                  |                  |              |
|                                           | white ppt        |                  |                  |                  |                  |                  |                  |              |
| $(\text{NH}_4)_2\text{S}$                 |                  |                  |                  |                  |                  |                  |                  |              |
|                                           |                  |                  |                  |                  |                  |                  |                  |              |
| $\text{NaI}$ (Petroleum ether)            |                  |                  |                  |                  |                  |                  |                  |              |
|                                           |                  |                  |                  |                  |                  |                  |                  |              |
| $\text{NH}_4\text{SCN}$                   |                  |                  |                  |                  |                  |                  |                  |              |
|                                           |                  |                  |                  |                  |                  |                  |                  |              |
| $\text{NaOH}$ (Limited amount)            |                  |                  |                  |                  |                  |                  |                  |              |
|                                           |                  |                  |                  |                  |                  |                  |                  |              |
| $\text{NaOH}$ (Excess amount)             |                  |                  |                  |                  |                  |                  |                  |              |
|                                           |                  |                  |                  |                  |                  |                  |                  |              |
| $\text{NH}_3(\text{aq})$ (Limited amount) |                  |                  |                  |                  |                  |                  |                  |              |
|                                           |                  |                  |                  |                  |                  |                  |                  |              |
| $\text{NH}_3(\text{aq})$ (Excess amount)  |                  |                  |                  |                  |                  |                  |                  |              |
|                                           |                  |                  |                  |                  |                  |                  |                  |              |

10. If  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  both are present, it is difficult to analyse. Outline a scheme to analyse in a mixture.
11.  $\text{HgS}$  is soluble in aqua regia forming  $\text{HgCl}_2$ . What happens if Cu turnings are added to  $\text{HgCl}_2$ ?
12. Sometimes it happens that when  $\text{H}_2\text{S}$  gas is passed into solution in dil.  $\text{HCl}$ , yellowish white turbidity appears. What do you conclude? What precautions are taken to check this turbidity?
13. If B (arsenic group) sulphides are soluble in YAS. If conc.  $\text{HCl}$  is added to this soluble portion, coloured ppt are formed. Write reactions.
14. Identify (A), (B), (C), (D) and (E). (A) (black) + dil.  $\text{HCl} \xrightarrow{\Delta} \text{(B)}(l) + \text{(C)}(g)$ . Gas (C) turns lead acetate paper black. (B) gives orange ppt (D) soluble in excess of  $\text{KI}$  forming (E).
15. Test tube (A) contains aqueous zinc acetate solution while test tube (B) contains aqueous zinc chloride solution. What happens if  $\text{H}_2\text{S}$  gas is passed into each solution?
16. (A) (colourless solution) gives white ppt (B) with  $\text{NaOH}$  solution but ppt dissolves in excess of  $\text{NaOH}$  forming (C). (C) does not give ppt with  $\text{H}_2\text{S}$  but on boiling with  $\text{NH}_4\text{Cl}$ , white ppt (B) appears. (A) also gives yellow ppt with  $\text{AgNO}_3$ . Identify (A), (B) and (C).
17. Colourless solution of (A) gives white ppt (B) with  $\text{AgNO}_3$  solution, soluble in aq  $\text{NH}_3$ . (A) also gives white ppt (C) with  $\text{NaOH}$  soluble in excess of it forming (D). (D) gives white ppt (E) with  $\text{H}_2\text{S}$ . Identify (A), (B), (C), (D) and (E).
18. A reagent can be used to identify  $\text{Ba}^{2+}$  and  $\text{Pb}^{2+}$  both. Name the reagent is.
19. Without going into systematic mixture analysis specify the test that can identify  $\text{Ba}^{2+}/\text{Ca}^{2+}/\text{Sr}^{2+}$
20. Teacher demonstrated that  $(\text{C}_2\text{O}_4^{2-})$  oxalate ion decolourised  $\text{MnO}_4^-/\text{H}^+$ . He also demonstrated that  $\text{Ca}^{2+}$  can be precipitated as  $\text{CaC}_2\text{O}_4$  (white) and these precipitate also decolourised  $\text{MnO}_4^-/\text{H}^+$ . While performing salt analysis quickly, a student performed this experiment without precipitation of  $\text{C}_2\text{O}_4^{2-}$  but salt given to him confirmed  $\text{MnO}_4^-/\text{H}^+$  test. He reported  $\text{C}_2\text{O}_4^{2-}$  but teacher awarded him zero. Can you explain positive  $\text{MnO}_4^-/\text{H}^+$  test?

21. Identify (A), (B), (C), (D) and (E).



(yellow)



Identify (A) to (H) and explain reactions.

23. Solution containing  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$  ions is called **magnesia mixture** and can be used to identify  $\text{PO}_4^{3-}$  ions. What can be other anion (acidic radical) which can be identified by this magnesia mixture?
24. You have following salts on your table in a lab.  $\text{KI}$ ,  $\text{HgI}_2$ ,  $\text{NaOH}$ ,  $\text{NH}_4\text{OH}$ ,  $\text{SnCl}_2$ .  
 (a) Select salts to prepare Nessler's reagent.  
 (b) Above reagent is used to identify which ion?  
 (c) Write reaction

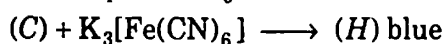
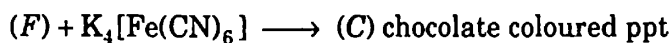
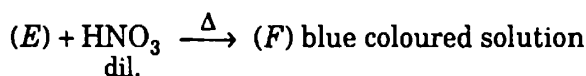
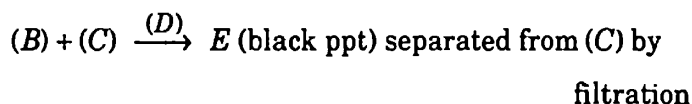
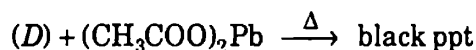
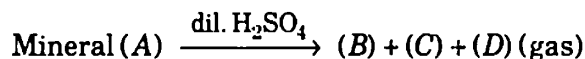
## Analytical Questions

1. A monomeric complex of cobalt gave the following results on analysis :

| $\text{Co}^{3+}$ | $\text{NH}_3$ | $\text{Cl}^-$ | $\text{SO}_4^{2-}$ |
|------------------|---------------|---------------|--------------------|
| % 21.24          | 24.77         | 12.81         | 34.65              |

The compound is diamagnetic and contains no other groups or elements, except water which might be present. What is probable formula of the compound? ( $\text{Co} = 59$ )

2. Identify (A) to (H) giving reactions taking place :



3. An aqueous solution of salt (A) gives a white crystalline precipitate (B) with  $\text{NaCl}$  solution. The filtrate gives a black precipitate (C) when  $\text{H}_2\text{S}$  is passed through it. Compound (B) dissolves in hot water and the solution gives yellow precipitate (D) on treatment with potassium iodide and on cooling. The compound (A) does not give any gas with dilute  $\text{HCl}$

but liberates a reddish brown gas on heating. Identify the compounds (A) to (D) giving the involved equations.

4. A white amorphous powder (A) when heated gives a colourless gas (B), which turns lime water milky and the residue (C) which is yellow when hot but white when cold. The residue (C) dissolves in dilute HCl and the resulting solution gives a white precipitate on addition of potassium ferrocyanide solution. (A) dissolves in dilute HCl with the evolution of a gas which is identical in all respects with (B). The solution of (A) as obtained above gives a white precipitate (D) on addition of excess of  $\text{NH}_4\text{OH}$  and on passing  $\text{H}_2\text{S}$ . Another portion of this solution gives initially a white precipitate (E) on addition of NaOH which dissolves in excess of it. Identify (A) to (E) and explain reactions.

5. Compound (A) is a light green crystalline solid. It gives the following tests :

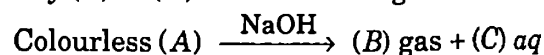
- It dissolves in dilute sulphuric acid. No gas is produced.
- A drop of  $\text{KMnO}_4$  is added to the above solution. The pink colour disappears.
- Compound (A) is heated strongly. Gases (B) and (C) with pungent smell came out. A brown residue (D) is left behind.
- The gas mixture [(B) and (C)] is passed into a dichromate solution. The solution turns green.
- The green solution from step (iv) gives a white precipitate (E) with a solution of barium nitrate.
- Residue (D) from (v) is heated on charcoal in reducing flame. It gives a magnetic substance.

Identify the compound (A) to (E).

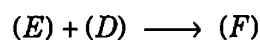
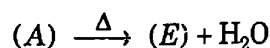
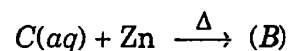
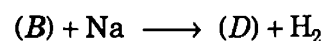
6. When 20.02 g of white solid (X) was heated, 4.4 g of acid gas (A) that turned lime water milky was driven off together with 1.8 g of a gas (B) which condenses to a colourless liquid. The solid (Y) that remained is dissolved in water to give an alkaline solution, with which excess barium chloride solution gave a white precipitate (Z). The precipitate effervesced with acid giving off carbon dioxide. Identify (A), (B) and (Y) and write down the equation for the thermal decomposition of (X).

7. A hydrated metallic salt (A), light green in colour, gives a white anhydrous residue (B) after being heated gradually. (B) is soluble in water and its aqueous solution reacts with NO to give a dark brown compound (C). (B) on strong heating gives a brown residue (D) and a mixture of two gases (E) and (F). The gaseous mixture, when passed through acidified permanganate, discharged the pink colour and when passed through acidified  $\text{BaCl}_2$  solution, gives a white precipitate. Identify (A), (B), (C), (D), (E) and (F).

8. Identify (A) to (G) in the following scheme :

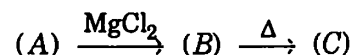


(alkaline due to excess NaOH added)



(G) contains 97.67% N, rest hydrogen.

9. 0.98 g of an acid (A) of phosphorus in 100 mL solution is 0.1 M and neutralises 300 mL of 0.1 N NaOH.



If 1.11 g of (C) is obtained from given (A), identify (A), (B) and (C).

10. An acid (A) can oxidise  $\text{I}^-$  to  $\text{I}_2$ . One mole of (A) can neutralise one mole of  $\text{Ca}(\text{OH})_2$  in aq solution. One mole of (A) in aqueous solution, on hydrolysis, gives two moles of another acid (B) and one mole of liquid (C). 0.98 g of acid (B) gives 2.33 g of white ppt (D) on reaction with excess of  $\text{BaCl}_2$ . Liquid (C) has oxidising as well as reducing property. (C) can decolourise  $\text{KMnO}_4/\text{H}^+$ , blackened oil paintings. Identify (A) to (D) and explain reactions.

11. A certain metal (A) is boiled in dilute nitric acid to give a salt (B) and an oxide of nitrogen (C). An aqueous solution of (B) with brine gives a precipitate (D) which is soluble in ammonium hydroxide. On adding aqueous solution of (B) to hypo solution, a white precipitate (E) is obtained. (E) on standing turns to a black compound (F). Identify (A) to (F).

12. An aqueous solution of a gas (X) gives the following reactions :

- It turns an acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution green.
- On boiling it with  $\text{H}_2\text{O}_2$ , cooling it and then adding an aqueous solution of  $\text{BaCl}_2$ , a precipitate insoluble in dilute hydrochloric acid is obtained.
- On passing  $\text{H}_2\text{S}$  in the solution a white turbidity is obtained.

Identify (X) and give equations for the reactions at steps (i), (ii) and (iii).

13. (a) A compound (X) imparts a golden yellow flame and shows the following reactions :
- Zinc powder when boiled with a concentrated aqueous solution of (X) dissolves and hydrogen is evolved.
  - When an aqueous solution of (X) is added to an aqueous solution of stannous chloride, a

white precipitate is obtained first which dissolves in excess of solution of (X).

Identify (X) and write equations for reactions at steps (i) and (ii).

(b) Write equations for the action of strong heat on borax and green vitriol.

14. A metal chloride (X) shows the following reactions :

- (i) When  $H_2S$  is passed in an acidified aqueous solution of (X), a black precipitate is obtained.
- (ii) The precipitate obtained at step (i) is not soluble in yellow ammonium sulphide.
- (iii) When a solution of stannous chloride is added to an aqueous solution of (X), a white precipitate is obtained which turns grey on addition of more of stannous chloride.
- (iv) When an aqueous solution of KI is added to an aqueous solution of (X), a red precipitate is obtained which dissolves on addition of excess of KI.

Identify (X) and write down the equations for the reactions at steps (i), (iii) and (iv).

15. (a) An aqueous solution of a gas (X) shows the following reactions :

- (i) It turns red litmus blue.
- (ii) When added in excess to a copper sulphate solution, a deep blue colour is obtained.
- (iii) On addition to a ferric chloride solution, a brown precipitate, soluble in dilute nitric acid, is obtained. Identify (X) and give equations for the reactions at steps (ii) and (iii).

(b) A certain compound (X) is used in laboratory for analysis. Its aqueous solution gives the following reactions :

- (i) On addition to a copper sulphate solution, a brown precipitate is obtained which turns white on addition of excess of  $Na_2S_2O_3$  solution.
- (ii) On addition to  $Ag^+$  ion solution, a yellow curdy precipitate is obtained which is insoluble in ammonium hydroxide.

Identify (X) and give equations for the reactions at step (i) and (ii).

16. A certain salt (X) gives the following tests :

- (i) Its aqueous solution is alkaline to litmus.
- (ii) On strongly heating it swells to give a glassy material.
- (iii) When concentrated sulphuric acid is added to a hot concentrated solution of (X), white crystals of a weak acid separate out.

Identify (X) and write down the chemical equations for reactions at steps (i), (ii) and (iii).

17. A certain compound (X) shows the following reactions :

- (i) When KI is added to an aqueous suspension of (X) containing acetic acid, iodine is liberated.

(ii) When  $CO_2$  is passed through an aqueous suspension of (X), the turbidity transforms to a precipitate.

(iii) When a paste of (X) in water is heated with ethyl alcohol, a product of anaesthetic use is obtained.

Identify (X) and write down chemical equations for reactions at steps (i), (ii) and (iii).

18. An aqueous solution of an inorganic compound (X) shows the following reactions :

- (i) It decolourises an acidified  $KMnO_4$  solution accompanied by the evolution of oxygen.
- (ii) It liberates iodine from an acidified potassium iodide solution.
- (iii) It gives a brown precipitate with alkaline  $KMnO_4$  solution with the evolution of oxygen.
- (iv) It removes black stains from old oil paintings.

Identify (X) and give chemical equations for the reactions at steps (i) to (iv).

19. Two solid laboratory reagents (A) and (B) give the following reactions :

**Compound (A) :**

- (i) On strongly heating it gives two oxides of sulphur.
- (ii) On adding aqueous NaOH solution to its aqueous solution, a dirty green precipitate is obtained which starts turning brown on exposure to air.

**Compound (B) :**

- (iii) It imparts green colour to the flame.
- (iv) Its solution does not give a precipitate on passing  $H_2S$ .
- (v) When it is heated with solid  $K_2Cr_2O_7$  and concentrated  $H_2SO_4$ , a red gas is evolved. The gas when passed in an aq NaOH solution turns it yellow.

Identify (A) and (B) and give chemical equations for reactions at step (i), (ii) and (v).

20. Identify (A) to (D) in following steps and give chemical equations :

- (i) A white amorphous powder (A) on strongly heating gives a colourless non-combustible gas (B) and solid (C).
- (ii) The gas (B) turns lime water milky and turbidity disappears with the passage of excess of gas.
- (iii) The solution (C) in dilute HCl gives a white precipitate with an aqueous solution of  $K_4[Fe(CN)_6]$ .
- (iv) The solution of (A) gives a white precipitate (D) on passing  $H_2S$  in presence of excess of  $NH_4OH$ .

- 21. (i) A black mineral (A) on heating in presence of air gives a gas (B).
- (ii) The mineral (A) on reaction with dilute  $H_2SO_4$  gives a gas (C) and solution of a compound (D).
- (iii) On passing gas (C) into an aqueous solution of (B), a white turbidity is obtained.

- (iv) The aqueous solution of compound (D) on reaction with potassium ferricyanide gives a blue compound (E). Identify (A) to (E) and give chemical equations for reactions at steps (i) to (iv).
22. An inorganic Lewis acid (X) shows the following reactions :
- It fumes in moist air.
  - The intensity of fumes increases when a rod dipped in  $\text{NH}_4\text{OH}$  is brought near it.
  - An acidic solution of (X) on addition of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  gives a precipitate which dissolves in  $\text{NaOH}$  solution.
  - An acidic solution of (X) does not give precipitate with  $\text{H}_2\text{S}$ . Identify (X) and give chemical equations for reactions steps (i) to (iii).
23. The certain inorganic compound (X) shows the following reactions :
- On passing  $\text{H}_2\text{S}$  through an acidified solution of (X), a brown precipitate is obtained.
  - The precipitate obtained at step (i) dissolves in excess of yellow ammonium sulphide.
  - On adding an aqueous solution of  $\text{NaOH}$  to a solution of (X), first a white precipitate is obtained which dissolves in excess of  $\text{NaOH}$ .
  - The aqueous solution of (X) reduces ferric chloride. Identify the cation of (X) and give chemical equations for reactions at steps (i), (ii) and (iv).
24. (i) An inorganic iodide (A) on heating with a solution of  $\text{KOH}$  gives a gas (B) and the solution of a compound (C).  
 (ii) The gas (B) on ignition in air gives a compound (D) and water.  
 (iii) Copper sulphate is finally reduced to the metal on passing (B) through its solution.  
 (iv) A precipitate of compound (E) is formed on reaction of (C) with  $\text{CuSO}_4$  solution. Identify (A) to (E) and explain reactions (i) to (iv).
25. A black mineral (A) is soluble in  $\text{NaCN}$  solution forming (B). On adding  $\text{Zn}$  into (B), metal (C) is formed. Metal (C) on boiling with  $\text{HNO}_3$  forms (D) which gives white ppt (E) with  $\text{NaCl}$ -soluble in  $\text{NH}_3$  solution. (A) can be obtained when (D) reacts with hypo. Identify (A) to (E).
26. (i) An inorganic compound (A) is formed on passing a gas (B) through a concentrated liquor containing sodium sulphide and sodium sulphite.  
 (ii) On adding (A) into a dilute solution of silver nitrate, a white precipitate appears which quickly changes into a black coloured compound (C).  
 (iii) On adding two or three drops of ferric chloride into the excess of solution of (A), a violet coloured compound (D) is formed. This colour disappears quickly.
- (iv) On adding a solution of (A) into the solution of cupric chloride, a white precipitate is first formed which dissolves on adding excess of (A) forming a compound (E).  
 Identify (A) to (E) and give chemical equations for the reactions at steps (i) to (iv).
27. (i) A black coloured compound (B) is formed on passing hydrogen sulphide through the solution of a compound (A) in  $\text{NH}_4\text{OH}$ .  
 (ii) (B) on treatment with hydrochloric acid and potassium chlorate gives (A).  
 (iii) (A) on treatment with potassium cyanide gives a buff coloured precipitate which dissolves in excess of this reagent forming a compound (C).  
 (iv) The compound (C) is changed into a compound (D) when its aqueous solution is boiled.  
 (v) The solution of (A) is treated with excess of sodium bicarbonate and then with bromine water. On cooling and shaking for sometime, a green colour of compound (E) is formed. No change is observed on heating.  
 Identify (A) to (E) and give chemical equations for the reactions at steps (i) to (v).
28. (i) An aqueous solution of a white coloured compound (A) on reaction with  $\text{HCl}$  gives a white precipitate of compound (B).  
 (ii) (B) becomes soluble in chlorine water with the formation of (C).  
 (iii) (C) reacts with  $\text{KI}$  to give a precipitate which becomes soluble in excess of it forming a compound (D). The compound (D) is used for detecting ammonium salts.  
 (iv) (B) and (C) both, on treatment with  $\text{SnCl}_2$  give a grey precipitate of (E).  
 (v) When conc.  $\text{H}_2\text{SO}_4$  is added slowly into a mixture of cold solutions of (A) and  $\text{FeSO}_4$ , a brown ring of compound (F) is formed. Identify (A) to (F) and give chemical equations for the reactions at steps (i) to (v).
29. (i) A blue coloured compound (A) on heating gives two products, (B) and (C).  
 (ii) A metal (D) is deposited on passing hydrogen through heated (B).  
 (iii) The solution of (B) in  $\text{HCl}$  on treatment with  $\text{K}_4[\text{Fe}(\text{CN})_6]$  gives a chocolate brown coloured precipitate of compound (E).  
 (iv) (C) turns lime water milky which disappears on continuous passage of (C) forming a compound (F).  
 Identify (A) to (F) and give chemical equations for the reactions at steps (i) to (iv).
30. (i) The yellow coloured precipitate of compound (A) is formed on passing  $\text{H}_2\text{S}$  through a neutral solution of a salt (B).  
 (ii) (A) is soluble in hot dilute  $\text{HNO}_3$ , but insoluble in yellow ammonium sulphide.

- (iii) The solution of (B) on treatment with small quantity of  $\text{NH}_3$  gives white precipitate which becomes soluble in excess of it forming a compound (C).
- (iv) The solution of (B) gives white precipitate with small concentration of KCN which becomes soluble in excess of this reagent forming a compound (D).
- (v) The solution of (D) on treatment with  $\text{H}_2\text{S}$  gives (A).
- (vi) The solution of (B) in dilute  $\text{HCl}$  on treatment with a solution of  $\text{BaCl}_2$  gives white precipitate of compound (E) which is insoluble in conc.  $\text{HNO}_3$ .

Identify (A) to (E) and give chemical equations for the reactions at steps (i) and (iii) to (vi).

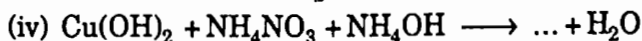
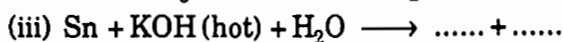
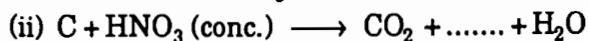
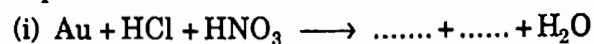
31. (i) An aqueous solution of a compound (A) is acidic towards litmus and (A) is sublimed at about  $300^\circ\text{C}$ .
- (ii) (A) on treatment with an excess of  $\text{NH}_4\text{SCN}$  gives a red coloured compound (B) and on treatment with a solution of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  gives a blue coloured compound (C).
- (iii) (A) on heating with excess of  $\text{K}_2\text{Cr}_2\text{O}_7$  in presence of concentrated  $\text{H}_2\text{SO}_4$  evolves deep red vapours of (D).
- (iv) On passing the vapours of (D) into a solution of  $\text{NaOH}$  and then adding the solution of acetic acid and lead acetate, a yellow precipitate of compound (E) is obtained.

Identify (A) to (E) and give chemical equations for the reactions at steps (ii) to (iv).

32. (a) Pyrolusite on heating with  $\text{KOH}$  in the presence of air gives a dark green compound (A). The solution of (A) on treatment with  $\text{H}_2\text{SO}_4$  gives a purple coloured compound (B), which gives following reactions :

- (i) KI on reaction with alkaline solution of (B) changes into a compound (C).
- (ii) The colour of the compound (B) disappears on treatment with the acidic solution of  $\text{FeSO}_4$ .
- (iii) With conc.  $\text{H}_2\text{SO}_4$  compound (B) gives (D) which can decompose to yield (E) and oxygen. Identify (A) to (E) and write balanced chemical equations for the formation of (A) and (B) and for the steps (i) to (iii).

- (b) Complete and balance the following chemical equations.



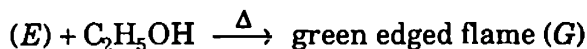
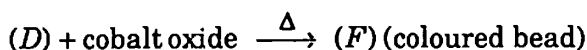
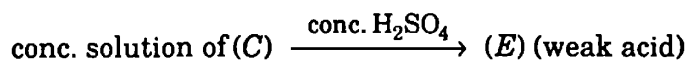
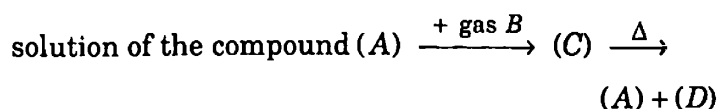
33. Unlabeled test tube contains solid  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  in one,  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  in another, and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  in the other. How could you find what is in each test tube

using chemical tests that involve only these compounds plus water?

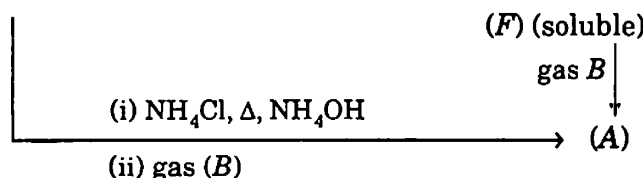
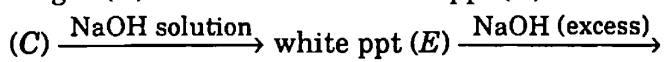
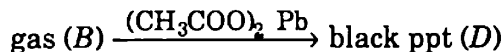
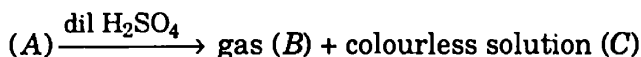
34. You are given three unlabeled test tubes. One test tube contains a solution of  $\text{Na}_2\text{SO}_4$ , the second contains a solution of  $\text{NaHSO}_4$  and the third contains a solution of  $\text{NaHSO}_3$ . Describe how you could identify the solutions.
35. Identify each of the following substances from the description.
- (a) A yellow solid that burns with a blue flame, giving off a gas with a choking odour.
  - (b) A white solid that reacts with water to give phosphoric acid.
  - (c) A colourless gas that poisons by attaching strongly to iron atoms in the haemoglobin of red blood cells.
  - (d) A hard, lustrous grey solid used as the base for solid state semiconductor devices.
36. Addition of  $\text{HCl} (aq)$  to a solution containing several different cations produces a white precipitate. The filtrate is removed and treated with  $\text{H}_2\text{S} (aq)$  in  $0.3 \text{ M HCl}$ . No precipitate forms. Which of the following conclusions is/are valid? Explain
- (a)  $\text{Ag}^+$  and/or  $\text{Hg}_2^{2+}$  probably present
  - (b)  $\text{Mg}^{2+}$  probably not present
  - (c)  $\text{Pb}^{2+}$  probably not present
  - (d)  $\text{Fe}^{2+}$  probably not present
37. Suppose you did a cation group I analysis and treated the chloride precipitate with  $\text{NH}_3 (aq)$ , without first treating it with hot water. What might you observe and what valid conclusions could you reach about cations present, cations absent, and cations in doubt?
38. Write net ionic equations for the following qualitative analysis procedures :
- (a) Precipitation of  $\text{PbCl}_2(s)$  from a solution containing  $\text{Pb}^{2+}(aq)$
  - (b) Dissolving of  $\text{Zn}(\text{OH})_2(s)$  in  $\text{NaOH}(aq)$ .
  - (c) Dissolving of  $\text{Fe}(\text{OH})_3(s)$  in  $\text{HCl}(aq)$ .
  - (d) Precipitation of antimony sulphide from a solution containing  $\text{H}_2\text{S}$  and the complex ion  $\text{SbCl}_4^-$ .
39. Identify A to E based on following observations and write balanced reactions therein :
- ```

(A)  $\xrightarrow{\text{neutral FeCl}_3 \text{ solution}}$  blood red colour (B)
    |
    |  $\xrightarrow{\text{dil. HCl, H}_2\text{S gas}}$  yellow ppt (C), (C dissolves in
    |                                     hot dil.  $\text{HNO}_3$  but insoluble in YAS)
    |
    |  $\xrightarrow{\text{aq NH}_3}$  white ppt soluble in excess of aq  $\text{NH}_3$ 
    |                                     forming (D)
    |
    |  $\xrightarrow{\text{aq KCN}}$  white ppt soluble in excess of aq KCN
    |                                     forming (E)
    |
    |  $\xrightarrow{\text{H}_2\text{S gas}}$ 
    |
    | yellow ppt (C)
  
```

40. Identify A to G based on following reactions :

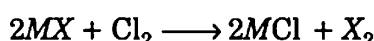


41. Colourless substance



What are (A), (B), (C), (D), (E) and (F) and explain reactions.

42. Element *M* is a shiny and highly reactive metal and element *X* is a highly reactive non-metal. They react to form a compound *MX*, a colourless brittle white solid. *MX* conducts electricity in aqueous solution and in molten state. When chlorine gas is bubbled through an aqueous solution, containing *MX*, a reddish-brown liquid appears and  $\text{Cl}^-$  ions are formed.



$\text{X}_2$  is decolourised by unsaturated hydrocarbon and aq solution of *MX* containing 1.19 g *MX* in 100 g  $\text{H}_2\text{O}$  freezes at  $-3.72^\circ\text{C}$ . Molar depression constant of  $\text{H}_2\text{O}$  is  $1.86^\circ\text{mol}^{-1}\text{kg}$ . Deduce the identity of the elements *M* and *X*.

43. An element *X* of group 2 reacts with  $\text{H}_2$  gas at  $200^\circ\text{C}$  to form a compound *Y*. When *Y* is heated to a higher temperature, it decomposes to the element *X* and hydrogen gas in the ratio of 559 mL  $\text{H}_2$  (measured at STP) for 1.00 g *X* reacted. *X* also combines with chlorine to form a compound *Z*, which contains 63.89 per cent by mass of chlorine. Deduce the identity of the element *X*, compound *Y* and *Z*.

44. A student is given samples of three elements *X*, *Y*, and *Z*, which could be an alkali metal, a member of group IVA, and a member of group VA. He makes the following observations :

Element *X* has a metallic lustre and conducts electricity. It reacts slowly with  $\text{HCl}$  to produce  $\text{H}_2$  gas. Element *Y* is a light-yellow solid that does not conduct electricity. Element *Z* has a metallic lustre

and conducts electricity. When exposed to air, slowly forms a white powder giving a basic solution in water. What can you conclude about the elements from these observations?

45. Deduce what you can about the nature of the following reactions :

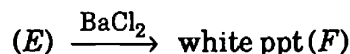
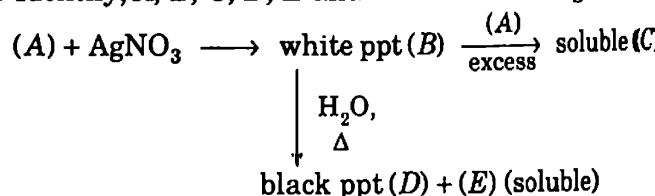
(a) One mole of  $\text{NH}_2\text{OH}$  reacts with two moles of  $\text{Ti(III)}$  in the presence of excess of alkali, and  $\text{Ti(III)}$  is converted into  $\text{Ti(IV)}$ .

(b) Silver phosphite,  $\text{Ag}_2\text{HPO}_3$ , is warmed with water, and dilute the silver is precipitated as the metal.

(c) When one mole of hypophosphorous acid,  $\text{H}_3\text{PO}_2$ , is warmed with excess of iodine in acidic solution, one mole of iodine is reduced; on making the solution alkaline, another mole of iodine is consumed.

46. The action of concentrated sulphuric acid on urea results in the production of a white crystalline solid *X* of formula  $\text{H}_3\text{NO}_3\text{S}$ , a monobasic acid. On treatment with sodium nitrite and dilute hydrochloric acid at  $0^\circ\text{C}$ , it liberates one mole of  $\text{N}_2$  per mol of *X*, and on addition of aqueous barium chloride, the resulting solution yields one mole of  $\text{BaSO}_4$  per mol of *X* taken. Deduce the structure of *X*.

47. Identify, *A*, *B*, *C*, *D*, *E* and *F* in the following :



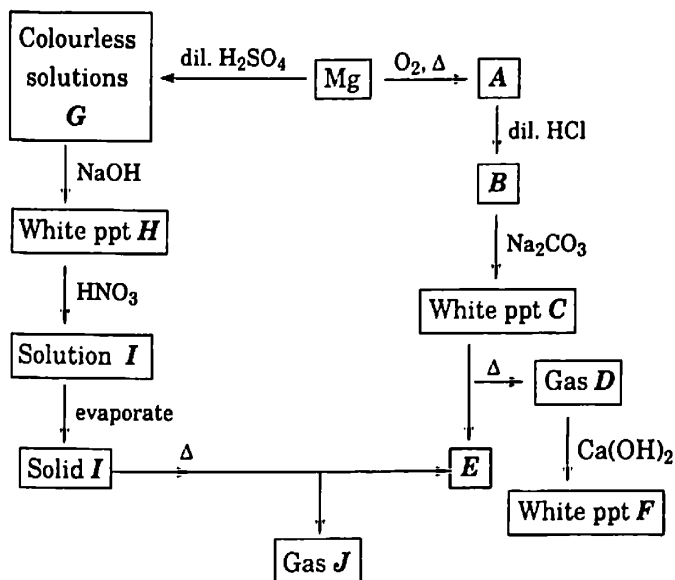
48. In strongly alkaline solution containing excess of barium ions, a solution containing 0.01587 g of  $\text{I}^-$  was treated with 0.1 molar  $\text{MnO}_4^-$  until a pink colour persisted in the solution : 10.0 mL of the  $\text{MnO}_4^-$  solution were required. Under these conditions  $\text{MnO}_4^-$  is converted into the sparingly soluble  $\text{BaMnO}_4$ . What is the product of the oxidation of iodide?

49. In neutral solution, one mole periodate ion,  $\text{IO}_4^-$ , reacts with excess of iodide to produce one mole of iodine; on acidification of the resulting solution, further three moles of iodine are liberated.

Derive equations of the reactions which occur under these conditions.

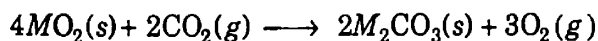
50. To prevent the formation of oxides, peroxides and superoxides, alkali metals are sometimes stored in an inert atmosphere. Which of the following gases should not be used for lithium? Why?  $\text{Ne}$ ,  $\text{Ar}$ ,  $\text{N}_2$ ,  $\text{K}$

51. The following are two reaction-schemes involving magnesium. Identify A to J based on the observations given :



52. When aqueous KCN is added to a solution of copper(II) sulphate, a white precipitate, soluble in an excess of KCN is formed. No precipitate is formed when  $\text{H}_2\text{S}$  is passed into it. Explain.

53. The reaction



is to be used to regenerate oxygen in space-craft. Discuss the choice of M among the alkali metals.

54. Write balanced chemical equations for the following reactions :

- A mixture of potassium dichromate and sodium chloride is heated with concentrated  $\text{H}_2\text{SO}_4$ .
- Aqueous solution of sodium nitrate is heated with zinc dust and caustic soda solution.
- Sodium iodate is added to a solution of sodium bisulphite.
- Iron reacts with cold dilute nitric acid.
- Potassium permanganate is added to a hot solution of manganous sulphate.

55. The gas liberated on heating a mixture of two salts with NaOH, gives a reddish brown precipitate with an alkaline solution of  $\text{K}_2\text{HgI}_4$ . The aqueous solution of the mixture on treatment with  $\text{BaCl}_2$  gives a white precipitate which is sparingly soluble in conc. HCl. On heating the mixture with  $\text{K}_2\text{Cr}_2\text{O}_7$  and conc.  $\text{H}_2\text{SO}_4$ , red vapours (A) are produced. The aqueous solution of the mixture gives a deep blue colouration (B) with potassium ferricyanide solution. Identify the radicals in the given mixture and write the balanced equations for the formation of (A) and (B).

56. Write balanced chemical equations for the following :

- Sodium nitrite is produced by absorbing the oxides of nitrogen in aqueous solution of washing soda.

- Nitrogen is obtained in the reaction of aqueous ammonia with potassium permanganate.
- Elemental phosphorus reacts with conc.  $\text{HNO}_3$  to give phosphoric acid.
- Sulphur is precipitated in the reaction of hydrogen sulphide with sodium bisulphite solution.
- Carbon dioxide is passed through a suspension of limestone in water.

57. Give reasons in one or two sentences for the following :

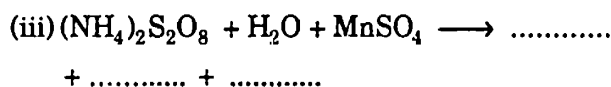
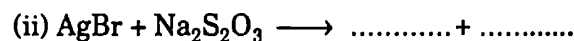
- The hydroxides of aluminium and iron are insoluble in water. However, NaOH is used to separate one from the other.
- Ammonium chloride is acidic in liquid ammonia solvent.

58. A light bluish green crystalline compound responds to the following tests :

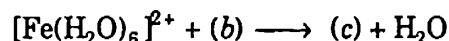
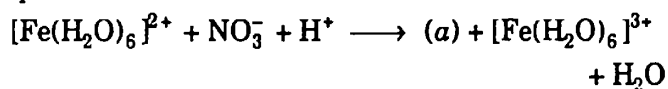
- Its aqueous solution gives a brown precipitate or colouration with alkaline  $\text{K}_2[\text{HgI}_4]$  solution.
- Its aqueous solution gives a blue colour with  $\text{K}_3[\text{Fe}(\text{CN})_6]$  solution.
- Its solution in hydrochloric acid gives a white precipitate with  $\text{BaCl}_2$  solution.

Identify the ions present and suggest the formula of the compound.

59. Complete and balance the following :



60. The acidic, aqueous solution of ferrous ion forms a brown complex in the presence of  $\text{NO}_3^-$  by the following two steps. Complete and balance the equations :



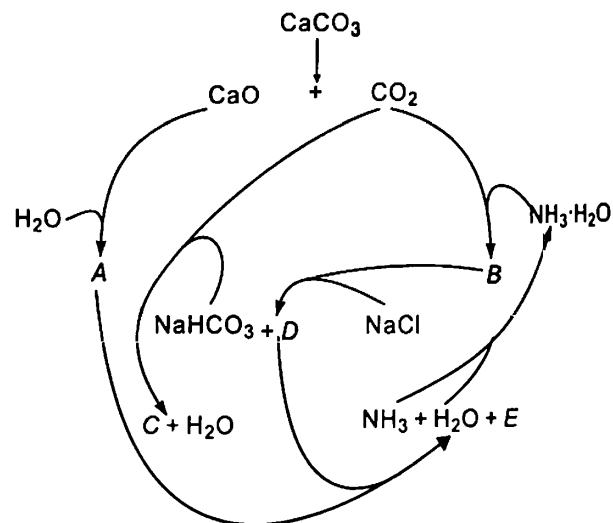
61. An orange solid (A) on heating gave a green residue (B), a colourless gas (C) and water vapours. The dry gas (C) on passing over heated Mg gave a white solid (D). (D) on reaction with water gave a gas (E) which formed dense white fumes with HCl. Identify (A) to (E) and give the reactions involved.

62. (A) is a binary compound of a univalent metal. 1.422 g of (A) reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid (B), that forms a hydrated double salt (C) with  $\text{Al}_2(\text{SO}_4)_3$ . Identify (A), (B) and (C).



63. When gas (A) is passed through dry KOH at low temperature, a deep red coloured compound (B) and a gas (C) are obtained. The gas A, on reaction with but-2-ene, followed by treatment with Zn/H<sub>2</sub>O yields acetaldehyde. Identify (A), (B) and (C).
64. A scarlet compound (A) is treated with conc. HNO<sub>3</sub> to give a chocolate brown precipitate (B). The precipitate is filtered and the filtrate is neutralised with NaOH. Addition of KI to the resulting solution gives a yellow precipitate (C). The precipitate (B) on warming with conc. HNO<sub>3</sub> in the presence of Mn(NO<sub>3</sub>)<sub>2</sub> produces a pink-coloured solution due to the formation of (D). Identify (A), (B), (C) and (D). Write the reactions in sequence.
65. (i) A white precipitate (B) is formed when a mineral (A) is boiled with Na<sub>2</sub>CO<sub>3</sub> solution.  
 (ii) The precipitate is filtered and the filtrate contains two compounds (C) and (D). The compound (C) is removed by crystallisation and when CO<sub>2</sub> is passed through the mother liquor left, (D) changes to (C).  
 (iii) The compound (C) on strong heating gives two compound (D) and (E).  
 (iv) E on heating with CoO forms blue colour bead (F). Identify (A) to (F).
66. A colourless inorganic salt (A) decomposes completely at about 250°C to give only two products (B) and (C) leaving no residue. The oxide (C) is a liquid at room temperature and neutral to moist litmus paper while the gas (B) is a neutral oxide. White phosphorus burns in excess of (B) to produce a strong white dehydrating agent (D). Write balanced equations for the reactions involved in the above process.
67. (a) Element (A) burns in nitrogen to give an ionic compound (B). Compound (B) reacts with water to give (C) and (D). A solution of (C) becomes 'milky' on bubbling carbon dioxide. Identify (A), (B), (C) and (D).  
 (b) Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction.
68. During the qualitative analysis of a mixture containing Cu<sup>2+</sup> and Zn<sup>2+</sup> ions, H<sub>2</sub>S gas is passed through an acidified solution containing these ions in order to test Cu<sup>2+</sup> alone. Explain briefly.
69. A white solid is either Na<sub>2</sub>O or Na<sub>2</sub>O<sub>2</sub>. A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid.  
 (i) Identify the substance and explain with balanced equation.  
 (ii) Explain what would happen to the red litmus if the white solid were the other compound.
70. An aqueous solution containing one mole of HgI<sub>2</sub> and two moles of NaI is orange in colour. On addition of excess NaI the solution becomes colourless. The orange colour reappears on subsequent addition of NaOCl. Explain with equations.
71. (a) In the following equation,  

$$(A) + 2(B) + H_2O \longrightarrow (C) + 2(D)$$
 [(A) = HNO<sub>2</sub>, (B) = H<sub>2</sub>SO<sub>3</sub>, (C) = NH<sub>2</sub>OH].  
 Identify (D). Draw the structures of (A), (B), (C) and (D).  
 (b) The Haber process can be represented by the following scheme :



Identify (A), (B), (C), (D) and (E).

## Exercise 2

### (Stage 2 : High Skill Problem Solving)

#### Only One Option Correct

1. Yellow coloured solution of FeCl<sub>3</sub> changes to light green when  
 (a) SnCl<sub>2</sub> is added (b) Zn is added  
 (c) H<sub>2</sub>S gas is passed (d) all true
2. Fe<sup>2+</sup> does not give blue colour with K<sub>4</sub>[Fe(CN)<sub>6</sub>] but on its reaction with (X), blue colour appears. (X) can be  
 (a) MnO<sub>4</sub><sup>-</sup>/H<sup>+</sup> (b) H<sub>2</sub>SO<sub>4</sub>  
 (c) NH<sub>3</sub> (d) HCl

3.  $\text{Fe}(\text{OH})_3$  and  $\text{Cr}(\text{OH})_3$  ppt are separated by  
 (a) Aq.  $\text{NH}_3$  (b)  $\text{HCl}$   
 (c)  $\text{NaOH}/\text{H}_2\text{O}_2$  (d)  $\text{H}_2\text{SO}_4$
4. Turnbull's blue and Prussian's blue respectively are  
 I.  $\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]^{2-}$  II.  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]$   
 III.  $\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]^-$  IV.  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$   
 (a) I, II (b) I, III  
 (c) III, IV (d) IV, III
5. Which of the following are soluble in excess of  $\text{NaOH}$   
 (X) :  $\text{As}_2\text{S}_3$ ; (Y) :  $\text{CuS}$ ; (Z) :  $\text{AlCl}_3$ ?  
 (a) X, Y, Z (b) Y, Z  
 (c) X, Z (d) X, Y
6. A mixture on heating gave a gas used as an anaesthetic, 1.1 g of gas occupies 0.56 L at NTP. Mixture contains  
 (a)  $\text{NaNO}_3 + \text{NH}_4\text{Cl}$  (b)  $\text{NaNO}_2 + \text{NH}_4\text{Cl}$   
 (c)  $\text{CaCO}_3 + \text{MgCO}_3$  (d)  $\text{NH}_4\text{Cl} + \text{Na}_2\text{SO}_4$
7. Aqueous solution contains  $\text{Zn}(\text{CH}_3\text{COO})_2$ ,  $\text{Cd}(\text{CH}_3\text{COO})_2$  and  $\text{Cu}(\text{CH}_3\text{COO})_2$ . On passing  $\text{H}_2\text{S}$  gas, there is a precipitation of ..... as sulphide  
 (a)  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  (b)  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$   
 (c)  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  (d)  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$
8. Ferric alum gives red colour with  $\text{NH}_4\text{SCN}$  due to formation of  
 (a)  $\text{Al}(\text{SCN})_3$  (b)  $[\text{Fe}(\text{SCN})_3]^-$   
 (c)  $\text{Fe}(\text{SCN})_3$  (d)  $[\text{Fe}(\text{SCN})]^{2+}$
9. Colourless salt (X)  $\xrightarrow{\Delta}$  (Y)  $\xrightarrow{\text{Cu}^{2+}, \Delta}$  coloured bead (Z). (X) can be  
 (a) borax (b) microcosmic salt  
 (c) both (a) and (b) (d) None of these
10.  $\text{KCl} + \text{conc } \text{H}_2\text{SO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} (\text{X}) \xrightarrow{\text{NaOH}} (\text{Y})$ . (X) is reddish brown coloured gas soluble in  $\text{NaOH}$  forming (Y). (X) and (Y) are  
 (a)  $\text{Cr}_2\text{OCl}_2$ ,  $\text{Na}_2\text{CrO}_3$  (b)  $\text{Cr}_2\text{O}_2\text{Cl}_2$ ,  $\text{Na}_2\text{CrO}_3$   
 (c)  $\text{CrO}_2\text{Cl}$ ,  $\text{Na}_2\text{CrO}_4$  (d)  $\text{CrO}_2\text{Cl}_2$ ,  $\text{Na}_2\text{CrO}_4$
11. Aqueous solution of  $\text{BaBr}_2$  gives yellow ppt with  
 (a)  $\text{K}_2\text{CrO}_4$  (b)  $\text{AgNO}_3$   
 (c) both (a) and (b) (d) None of these
12.  $\text{Cr}_2\text{O}_7^{2-} \xrightleftharpoons[\text{pH} = y]{\text{pH} = x} \text{CrO}_4^{2-}$ . This change is based on change in pH. Probable values of x and y can be  
 (a) 8, 6  
 (b) 8, 10  
 (c) 4, 6  
 (d) change is independent of pH
13.  $\text{H}_2\text{S}$  would separate the following at  $\text{pH} < 7$   
 (a)  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$  (b)  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$   
 (c)  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  (d)  $\text{Cu}^{2+}$ ,  $\text{As}^{3+}$
14. Solution of (X) in dil.  $\text{HCl} + \text{H}_2\text{O} \longrightarrow$  white turbidity. (X)  $\xrightarrow{\text{H}_2\text{S}/\text{HCl}}$  black ppt (Y). (Y) is soluble in  
 (a)  $\text{H}_2\text{SO}_4$  (b)  $\text{YAS}$   
 (c)  $\text{HNO}_3$  (d)  $\text{HCl}$
15.  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{conc. } \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 + \text{ether} \longrightarrow$  blue perchromic anhydride (in ethereal layer). Blue colour is due to  
 (a)  $\text{CrO}_3$  (b)  $\text{H}_2\text{CrO}_4$   
 (c)  $\text{H}_2\text{Cr}_2\text{O}_3$  (d)  $\text{CrO}_5$
16. There is foul smell in presence of moisture with  
 (a)  $\text{AlCl}_3$  (b)  $\text{Al}_2(\text{SO}_4)_3$   
 (c)  $\text{FeS}$  (d)  $\text{FeSO}_4$
17.  $\text{AgNO}_3$  gives white ppt with hypo changing to black after sometime. Black ppt is of  
 (a)  $\text{Ag}_2\text{S}_2\text{O}_3$  (b)  $\text{Ag}_2\text{SO}_4$   
 (c)  $\text{Ag}_2\text{S}_4\text{O}_6$  (d)  $\text{Ag}_2\text{S}$
18.  $\text{SO}_2$  and  $\text{CO}_2$  both turn lime water (A) milky,  $\text{SO}_2$  also turns  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$  (B) green while  $\text{O}_2$  is soluble in pyrogallol (C) turning it black. These gases are to be detected in order by using these reagents. The order is  
 (a) (A), (B), (C) (b) (B), (C), (A)  
 (c) (B), (A), (C) (d) (A), (C), (B)
19. Aluminium sulphate (X) is slightly insoluble in water. It is converted into soluble sodium sulphate by using  $\text{Na}_2\text{CO}_3$  in the preparation of sodium carbonate extract. Moles of (Y), required for complete conversion of 1 mole of (X) into soluble sulphate, is  
 (a) 1 (b) 2  
 (c) 3 (d) 4
20.  $\text{CoCl}_2$  gives blue colour with  $\text{NH}_4\text{SCN}$  in ethereal layer due to formation of  
 (a)  $(\text{NH}_4)_2[\text{Co}(\text{SCN})_4]$  (b)  $(\text{NH}_4)_4[\text{Co}(\text{SCN})_6]$   
 (c)  $(\text{NH}_4)_3[\text{Co}(\text{SCN})_6]$  (d)  $(\text{NH}_4)[\text{Co}(\text{SCN})_4]$
21.  $\text{HgCl}_2 + \text{excess of KI} \longrightarrow (\text{A}) \xrightarrow{\text{NH}_3/\text{NaOH}} (\text{B})$ . (A) and (B) respectively are  
 (a)  $\text{K}_2\text{HgI}_4$  (Nessler's reagent),  $\text{O} \begin{array}{c} \text{Hg} \\ \diagup \quad \diagdown \\ \text{Hg} \end{array} \text{NH}_2\text{I}$   
 (X) (Iodide of Millon's base)  
 (Y)
- (b) (Y), (X)  
 (c) both (X)  
 (d) both (Y)
22.  $\text{NH}_4\text{SCN}$  can be used to test one or more out of  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$   
 (a)  $\text{Fe}^{3+}$  only (b)  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$   
 (c)  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$  (d) all of these

23.  $K_4[Fe(CN)_6]$  can be used to detect one or more out of  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$   
 (a)  $Fe^{2+}$ ,  $Fe^{3+}$  (b)  $Fe^{3+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$   
 (c) all but  $Fe^{3+}$  (d) all but  $Fe^{2+}$
24. Aqueous solution containing one mole borax reacts with two moles of acids. This is because of  
 (a) formation of 2 moles of  $B(OH)_3$  only  
 (b) formation of 2 moles of  $[B(OH)_4]^-$  only  
 (c) formation of 1 mole each of  $B(OH)_3$  and  $[B(OH)_4]^-$   
 (d) formation of 2 mol each of  $[B(OH)_4]^-$  and  $B(OH)_3$ , of which only  $[B(OH)_4]^-$  reacts with acid.
25.  $Ag_2S$  is soluble in  $NaCN$  due to formation of  
 (a)  $Na[Ag(CN)_2]$  (b)  $Ag(CN)_2$   
 (c)  $Na_2[Ag(CN)_3]$  (d)  $Na_2[Ag(CN)_2]$
26. Match the substances given in **B** based on reactions given in **A** and select correct answer from the alternate

| A (Reactions) |                                                                                                  | B (Substances) |           |
|---------------|--------------------------------------------------------------------------------------------------|----------------|-----------|
| I:            | a white, waxy solid, normally stored under water because it spontaneously inflames in air        | P:             | $HNO_3$   |
| II:           | a viscous liquid that reacts with table sugar, giving a charred mass                             | Q:             | $Cl_2$    |
| III:          | an acid that reacts with copper metal, releasing brown fumes                                     | R:             | P         |
| IV:           | a pale greenish yellow gas that dissolves in aqueous $NaOH$ to give a solution used as a bleach. | S:             | $H_2SO_4$ |

- |       |    |     |    |       |    |     |    |
|-------|----|-----|----|-------|----|-----|----|
| I     | II | III | IV | I     | II | III | IV |
| (a) P | Q  | R   | S  | (b) S | R  | Q   | P  |
| (c) R | S  | P   | Q  | (d) S | R  | P   | Q  |
27.  $Cu^{2+}$  and  $Ag^+$  are both present in the same solution. To precipitate one of the ions and leave the other in solution, add  
 (a)  $H_2S(aq)$  (b)  $HCl(aq)$   
 (c)  $HNO_3(aq)$  (d)  $NH_4NO_3(aq)$
28. The addition of  $K_2CO_3(aq)$  to the following solutions is expected to produce a precipitate in every case but one. That one is  
 (a)  $BaCl_2(aq)$  (b)  $CaBr_2(aq)$   
 (c)  $Na_2SO_4(aq)$  (d)  $Pb(NO_3)_2(aq)$
29. A large excess of  $MgF_2(s)$  is maintained in contact with 1.00 L of pure water to produce a saturated solution. When an additional 1.00 L of pure water is added to the solid-liquid mixture and equilibrium re-established, compared to its value in the original saturated solution  $[Mg^{2+}]$  will be  
 (a) the same (b) twice as large  
 (c) three as large (d) half as large

30. To increase the molar solubility of  $CaCO_3(s)$  in saturated aqueous solution add  
 (a) more water (b)  $Na_2CO_3$   
 (c)  $NaOH$  (d)  $NaHSO_4$
31.  $Cu(OH)_2$  is highly soluble in all of the following except one. The exception is  
 (a)  $H_2O$  (b)  $NH_3(aq)$   
 (c)  $HCl(aq)$  (d)  $HNO_3(aq)$
32. To increase significantly the concentration of free  $Zn^{2+}$  ion is a solution of the complex ion  $[Zn(NH_3)_4]^{2+}$   
 $Zn^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Zn(NH_3)_4]^{2+}(aq)$   
 add to the solution some  
 (a)  $H_2O$  (b)  $HCl(aq)$   
 (c)  $NH_3(aq)$  (d)  $NH_4Cl(aq)$
33. The best way to ensure complete precipitation from saturated  $H_2S(aq)$  of a metal ion  $M^{2+}$ , as its sulphide,  $MS(s)$ , is to  
 (a) add an acid  
 (b) increase  $[H_2S]$  in solution  
 (c) raise the pH  
 (d) heat the solution
34. Of the following solutions the one that is acidic is  
 (a)  $ZnSO_4(aq)$  (b)  $NaAl(OH)_4(aq)$   
 (c)  $NaHCO_3(aq)$  (d)  $KNO_3(aq)$
35. Of the following oxides, all are soluble in  $NaOH(aq)$  except  
 (a)  $ZnO$  (b)  $Al_2O_3$   
 (c)  $Fe_2O_3$  (d)  $SnO_2$
36. Marsh test is used for detecting  
 (a) As (b) Zn  
 (c) Al (d)  $CH_4$
37. With  $MnO$ , colour of the bead in sodium carbonate-bead test is  
 (a) pink (b) black  
 (c) yellow (d) green
38. With  $Cr_2O_3$ , colour of the bead in sodium carbonate-bead test is  
 (a) red (b) blue  
 (c) yellow (d) green
39. Colourless salt (A) + dil.  $H_2SO_4$  +  $KI \rightarrow$  blue colour with solution (A) can be  
 (a)  $K_2Cr_2O_7$  (b)  $MnO_2$   
 (c)  $NH_4NO_2$  (d)  $NH_4Cl$
40. Three test tubes A, B, C contain  $Pb^{2+}$ ,  $Hg_2^{2+}$  and  $Ag^+$  (but unknown). To each aqueous solution  $NaOH$  is added in excess. Following changes occur.  
 A : Black ppt

B : Brown ppt

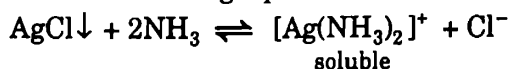
C : White ppt but dissolves in excess of NaOH

A, B and C contain respectively

(a)  $\text{Pb}^{2+}$ ,  $\text{Hg}_2^{2+}$  and  $\text{Ag}^+$  (b)  $\text{Hg}_2^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$

(c)  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}_2^{2+}$  (d)  $\text{Ag}^+$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Pb}^{2+}$

41. Consider the following equilibrium



White ppt of AgCl appears on adding

(a)  $\text{NH}_3$  (b) aq NaCl

(c) aq  $\text{HNO}_3$  (d) aq  $\text{NH}_4\text{Cl}$

42.  $\text{Ag}_2\text{CrO}_4$  ppt is soluble in

(a) dil.  $\text{HNO}_3$  (b) aq  $\text{NH}_3$

(c) both (a) and (b) (d) None of these

43. A mixture contains  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Ni}^{2+}$ . Following steps have been adopted but written in disorder

I : Filter, boil off  $\text{H}_2\text{S}$  gas and add  $\text{NH}_4\text{Cl}$ , heat and add  $\text{NH}_4\text{OH}$ .

II : Filter, add  $\text{NH}_4\text{OH}$  and pass  $\text{H}_2\text{S}$  gas.

III : Pass  $\text{H}_2\text{S}$  gas into acidified solution of mixture.

Steps will be used in the following order

(a) I, II, III (b) III, I, II

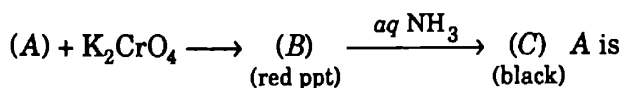
(c) III, II, I (d) I, III, II

44. KI gives precipitate with all the cations given

(a)  $\text{Ag}^+$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Pb}^{2+}$  (b)  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$

(c)  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  (d)  $\text{Ag}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$

45. Aqueous solution of salt



(a)  $\text{AgNO}_3$  (b)  $\text{Pb}(\text{NO}_3)_2$

(c)  $\text{Hg}_2(\text{NO}_3)_2$  (d)  $\text{Ca}(\text{NO}_3)_2$

46. A is a colourless substance. Aqueous solution of A gives reddish-orange ppt with KI; ppt dissolves in excess of KI forming a colourless solution. If  $\text{NH}_4\text{Cl}$  and NaOH solution is added to this colourless solution reddish brown ppt is formed. Substance A is

(a) Epsom salt (b) Mohr's salt

(c) Calomel (d) Corrosive sublimate

47.  $\text{CoS}$  (black) obtained in group IV of salt analysis is dissolved in aqua regia, treated with an excess of  $\text{NaHCO}_3$  and then  $\text{Br}_2$  water is added. An apple green coloured stable complex is formed. It is

(a) sodium cobaltocarbonate

(b) sodium cobaltibromide

(c) sodium cobalticarbonate

(d) sodium cobaltobromide

48. Which of the following salt does not give positive test for nitrate ion?

(a)  $\text{KNO}_3$  (b)  $\text{NaNO}_3$

(c)  $\text{Pb}(\text{NO}_3)_2$  (d)  $\text{Mg}(\text{NO}_3)_2$

49. An aqueous solution of  $\text{MCl}_2$  containing excess KCN, when treated with  $\text{H}_2\text{S}$  will precipitate MS only if 'M' is

(a) Ni (b) Co

(c) Cu (d) Cd

50. Borax on heating strongly above its melting point melts to a liquid, which then solidifies to a transparent mass commonly known as borax-bead. The transparent glassy mass consists of

(a) sodium pyroborate

(b) boric anhydride

(c) sodium metaborate

(d) boric anhydride and sodium metaborate

51. If  $\text{CO}_2$  gas is passed into aq  $\text{Na}_2\text{CrO}_4$  yellow solution

(a) aq  $\text{Na}_2\text{Cr}_2\text{O}_7$  (orange) solution is formed

(b) aq  $\text{Cr}_2(\text{CO}_3)_2$  is formed

(c)  $\text{Cr}(\text{OH})_3$  is precipitated

(d) no action

52. A mixture of two colourless substances was dissolved in water. When gaseous  $\text{Cl}_2$  was passed through the solution, a deep brown colour developed. Addition of  $\text{BaCl}_2$  or NaOH to the original solution give a white precipitate. The mixture contained

(a)  $\text{NaNO}_3$  and  $\text{AlCl}_3$

(b)  $\text{NaBr}$  and  $\text{KCl}$

(c)  $\text{MgI}_2$  and  $\text{MgSO}_4$

(d)  $\text{BaSO}_4$  and  $\text{PbCl}_2$

53. Four test tubes containing dil.  $\text{HCl}$ ,  $\text{BaCl}_2$ ,  $\text{CdCl}_2$  and  $\text{KNO}_3$  solution. Which of the following will identify  $\text{BaCl}_2$ ?

(a) Dil.  $\text{H}_2\text{SO}_4$  (b)  $\text{K}_2\text{CrO}_4$

(c)  $\text{FeSO}_4/\text{H}_2\text{SO}_4$  (d)  $\text{AgNO}_3$

54. The ion most difficult to remove as a precipitate is

(a)  $\text{Ag}^+$  (b)  $\text{NH}_4^+$

(c)  $\text{Fe}^{3+}$  (d)  $\text{Cu}^{2+}$

55. A colourless gas is dissolved in water and the resulting solution turns red litmus blue, the gas may have been which one of the following?

(a)  $\text{HCl}$  (b)  $\text{H}_2\text{S}$

(c)  $\text{SO}_2$  (d)  $\text{NH}_3$

56. A substance that will deliquesce in the normal laboratory atmosphere is:

(a)  $\text{CuSO}_4$  (b) NaOH

(c)  $\text{SiO}_2$  (d) all of these

57. A salt which will turn dark on exposure to sunlight has the formula

(a)  $\text{K}_2\text{C}_2\text{O}_4$  (b)  $\text{CaCl}_2$

(c)  $\text{AgCl}$  (d)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]$

58. What would you observe if you add with shaking, excess dil. NaOH solution to  $\text{ZnCl}_2$  solution?
- A white ppt
  - A white ppt which later dissolves
  - A green ppt
  - A green ppt which later dissolves
59. A mixture is known to contain  $\text{NO}_3^-$  and  $\text{NO}_2^-$ . Before performing **Ring Test** for  $\text{NO}_3^-$ , the aqueous solution should be made free of  $\text{NO}_2^-$ . This is done by heating aqueous extract with
- conc.  $\text{HNO}_3$
  - dil.  $\text{HNO}_3$
  - urea
  - zinc dust
60. A suspension containing insoluble substances  $\text{ZnS}$ ,  $\text{CuS}$ ,  $\text{Hg}_2\text{S}$ ,  $\text{Ag}_2\text{S}$ , and  $\text{FeS}$ , is treated with 2N HCl. On filtering, the filtrate contained appreciable amounts of which one of the following groups?
- Zinc and mercury
  - Silver and iron
  - Copper and mercury
  - Zinc, copper and iron
61. The compound thioacetamide has been into analytical chemistry to replace which one of the following reagents?
- $\text{H}_2\text{S}$
  - DMG
  - YAS
  - $(\text{NH}_4)_2\text{C}_2\text{O}_4$
62. Some white colourless crystals are heated. A cracking sound is heard and brown fumes are given off. The residue is yellow-brown in colour. When a glowing splinter is held in the fumes, it is relighted. The fumes consists of
- $\text{O}_2$
  - $\text{NO}_2$
  - $\text{Cl}_2$
  - $\text{NO}_2$  and  $\text{O}_2$
63. A yellow solid known to be a single compound is completely insoluble in hot water but dissolves in hot dilute HCl to give an orange solution. When this solution is cooled, a white crystalline ppt is formed. This white ppt redissolves on heating the solution. The compound is
- $\text{Fe}(\text{OH})_3$
  - $\text{PbCrO}_4$
  - $\text{K}_2\text{CrO}_4$
  - $\text{Co}(\text{OH})_2$
64. 'X' is a colourless salt giving following reactions:
- $\xleftarrow{\text{NaOH}}$

X

white ppt  
but dissolves in  
excess of NaOH

$\downarrow \text{NH}_4\text{OH}/\text{H}_2\text{S}$

X

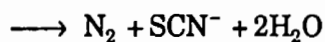
White ppt.

$\xrightarrow{\text{AgNO}_3/\text{HNO}_3}$

White ppt.  
soluble in  
aq.  $\text{NH}_3$
- X can be
- $\text{AlCl}_3$
  - $\text{ZnCl}_2$
  - $\text{Zn}(\text{CH}_3\text{COO})_2$
  - $\text{ZnBr}_2$
65. A mixture upon adding conc.  $\text{H}_2\text{SO}_4$  gives orange red fumes. It may contain the anion pair
- $\text{CrO}_4^{2-} + \text{Cl}^-$
  - $\text{Br}^- + \text{Cl}^-$
  - $\text{NO}_3^- + \text{Cl}^-$
  - $\text{CrO}_4^{2-} + \text{NO}_3^-$
66. When calomel reacts with  $\text{NH}_4\text{OH}$ , we get
- $\text{Hg}(\text{NH}_2)\text{Cl} + \text{Hg}$
  - $\text{NH}_2-\text{Hg}-\text{Hg}-\text{Cl}$
  - $\text{Hg}_2\text{O}$
  - $\text{HgO}$
67. When a substance A reacts with water it produces a combustible gas B and a solution of substance C in water. When another substance D reacts with this solution of C, it also produces the same gas B on warming but D can produce gas B on reaction with dilute sulphuric acid at room temperature. A imparts a deep golden yellow colour to a smokeless flame of Bunsen burner. A, B, C and D, respectively are
- Na,  $\text{H}_2$ , NaOH, Zn
  - K,  $\text{H}_2$ , KOH, Al
  - $\text{CaH}_2$ ,  $\text{Ca}(\text{OH})_2$ , Sn
  - $\text{CaC}_2$ ,  $\text{C}_2\text{H}_2$ ,  $\text{Ca}(\text{OH})_2$ , Fe
68. In the separation of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  in 2nd group of qualitative analysis of cations tetrammine copper(II) sulphate and tetraammine cadmium(II) sulphate react with KCN to form the corresponding cyanide complexes, which one of the following pairs of the complexes and their relative stabilities enables the separation of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ ?
- $\text{K}_3[\text{Cu}(\text{CN})_4]$  : less stable and  $\text{K}_2[\text{Cd}(\text{CN})_4]$  : more stable
  - $\text{K}_3[\text{Cu}(\text{CN})_4]$  : more stable and  $\text{K}_2[\text{Cd}(\text{CN})_4]$  : less stable
  - $\text{K}_2[\text{Cu}(\text{CN})_4]$  : less stable and  $\text{K}_2[\text{Cd}(\text{CN})_4]$  : more stable
  - $\text{K}_2[\text{Cu}(\text{CN})_4]$  : more stable and  $\text{K}_2[\text{Cd}(\text{CN})_4]$  : less stable
69. Chemical A is used for softening of water to remove temporary hardness. A reacts with sodium carbonates to produce caustic soda. When  $\text{CO}_2$  is bubbled through 'A' it turns cloudy. Chemically 'A' is
- CaO
  - $\text{CaCO}_3$
  - $\text{Ca}(\text{HCO}_3)_2$
  - $\text{Ca}(\text{OH})_2$
70. The solution of sodium meta aluminate on boiling with ammonium chloride gives a white precipitate of
- $\text{Al}_2\text{O}_3$
  - $\text{AlCl}_3$
  - $\text{Al}(\text{OH})_3$
  - $\text{NaAl}(\text{OH})_4$
71. Nitrite ( $\text{NO}_2^-$ ) interferes in the 'ring-test' of nitrate ( $\text{NO}_3^-$ ). Some of the following reagents can be used for the removal of nitrite.
- $\text{NH}_4\text{Cl}$
  - $(\text{NH}_2)_2\text{CS}$  (thiourea)
  - $\text{NH}_2\text{SO}_3\text{H}$  (sulphamic acid)
  - Sulphanilic acid
- Correct choice is
- I, II
  - I, II, IV
  - I, II, III
  - I, III, IV

72. Consider following reaction

Nitrite + acetic acid + thiourea



Formation of the product in the above reaction can be identified by

- (a)  $\text{FeCl}_3/\text{dil. HCl}$  when blood red colour appears
- (b)  $\text{FeCl}_3/\text{dil. HCl}$  when blue colour appears
- (c)  $\text{K}_2\text{Cr}_2\text{O}_7/\text{HCl}$  when green colour appears
- (d)  $\text{KMnO}_4/\text{HCl}$  when colourless solution is formed

73. Zinc pieces are added to acidified solution of  $\text{SO}_3^{2-}$ .

Gas liberated can

- (a) turn lead acetate paper black
- (b) turn lime water milky
- (c) give both of the above tests
- (d) give none of the above tests

74. Sodium nitroprusside turns purple when it is exposed in the atmosphere of

- (a) CO
- (b)  $\text{H}_2\text{S}$
- (c)  $\text{SO}_2$
- (d)  $\text{CO}_2$

75. Select correct statement(s).

- (a)  $\text{Ag}_2\text{S}_2\text{O}_3$  appears as white precipitate when  $\text{Na}_2\text{S}_2\text{O}_3$  reacts with  $\text{AgNO}_3$
- (b)  $\text{Ag}_2\text{S}_2\text{O}_3$  is unstable turning black on standing due to formation of  $\text{Ag}_2\text{S}$
- (c)  $\text{S}_2\text{O}_3^{2-}$  can form soluble complex  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$  with  $\text{Ag}^+$
- (d) All the above are correct statements

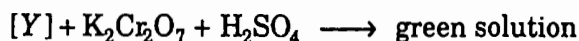
76. A gas X is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas Y. Identify X and Y

- (a)  $X = \text{CO}_2$ ,  $Y = \text{Cl}_2$
- (b)  $X = \text{Cl}_2$ ,  $Y = \text{CO}_2$
- (c)  $X = \text{Cl}_2$ ,  $Y = \text{H}_2$
- (d)  $X = \text{H}_2$ ,  $Y = \text{Cl}_2$

77. An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a

- (a)  $\text{Hg}^{2+}$  salt
- (b)  $\text{Cr}^{2+}$  salt
- (c)  $\text{Ag}^+$  salt
- (d)  $\text{Pb}^{2+}$  salt

78.  $[\text{X}] + \text{H}_2\text{SO}_4 \longrightarrow [\text{Y}]$  a colourless gas with irritating smell



$[\text{X}]$  and  $[\text{Y}]$  are

- (a)  $\text{SO}_3^{2-}$ ,  $\text{SO}_2$
- (b)  $\text{Cl}^-$ ,  $\text{HCl}$
- (c)  $\text{S}^{2-}$ ,  $\text{H}_2\text{S}$
- (d)  $\text{CO}_3^{2-}$ ,  $\text{CO}_2$

79. For  $\text{H}_3\text{PO}_3$ , the correct choice is

- (a)  $\text{H}_3\text{PO}_3$  is dibasic and reducing
- (b)  $\text{H}_3\text{PO}_3$  is dibasic and non-reducing
- (c)  $\text{H}_3\text{PO}_3$  is tribasic and reducing
- (d)  $\text{H}_3\text{PO}_3$  is tribasic and non-reducing

80. A sodium salt of an unknown anion when treated with  $\text{MgCl}_2$  gives white precipitate only boiling. The anion is

- (a)  $\text{SO}_4^{2-}$
- (b)  $\text{HCO}_3^-$
- (c)  $\text{CO}_3^{2-}$
- (d)  $\text{NO}_3^-$

81. A metal nitrate reacts with KI to give a black precipitate which on addition of excess of KI converts into orange colour solution. The cation of metal nitrate is

- (a)  $\text{Hg}^{2+}$
- (b)  $\text{Bi}^{3+}$
- (c)  $\text{Pb}^{2+}$
- (d)  $\text{Cu}^+$

82. A solution when diluted with  $\text{H}_2\text{O}$  and boiled, gives a white precipitate. On addition of excess  $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ , the volume of precipitate decreases leaving behind a white gelatinous precipitate. Identify the precipitate which dissolves in  $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$

- (a)  $\text{Zn}(\text{OH})_2$
- (b)  $\text{Al}(\text{OH})_3$
- (c)  $\text{Mg}(\text{OH})_2$
- (d)  $\text{Ca}(\text{OH})_2$

83.  $\text{CuSO}_4$  is decolourised on addition of KCN, the product is

- (a)  $[\text{Cu}(\text{CN})_4]^{2-}$
- (b)  $[\text{Cu}(\text{CN})_4]^{3-}$
- (c)  $\text{Cu}(\text{CN})_2$
- (d)  $\text{CuCN}$

84. A solution of a metal ion when treated with KI gives a red precipitate which dissolves in excess KI to give a colourless solution. Moreover, the solution of metal ion on treatment with a solution of cobalt(III) thiocyanate gives rise to a deep blue crystalline precipitate. The metal ion is

- (a)  $\text{Pb}^{2+}$
- (b)  $\text{Hg}^{2+}$
- (c)  $\text{Cu}^{2+}$
- (d)  $\text{Co}^{2+}$

85. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and  $\text{H}_2\text{SO}_4$ , in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of

- (a)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
- (b)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$
- (c)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_2$
- (d)  $\text{Fe}[\text{Fe}(\text{CN})_6]_3$

86. A dark violet colour mixture in presence of dil. HCl changes to pale yellow solution. Mixture may contain

- (a)  $\text{MnO}_4^-$ ,  $\text{Fe}^{2+}$
- (b)  $\text{MnO}_4^-$ ,  $\text{C}_2\text{O}_4^{2-}$
- (c)  $\text{I}^-$ ,  $\text{C}_2\text{O}_7^{2-}$
- (d) none is correct

87. Mixture is initially orange in colour. When solution is prepared in dil. acid, it changes to dark brown colour. Mixture contains

- (a)  $\text{HgI}_2$ ,  $\text{C}_2\text{O}_7^{2-}$
- (b)  $\text{I}^-$ ,  $\text{C}_2\text{O}_7^{2-}$
- (c)  $\text{I}^-$ ,  $\text{Cu}^{2+}$
- (d)  $\text{I}^-$ ,  $\text{SO}_3^{2-}$

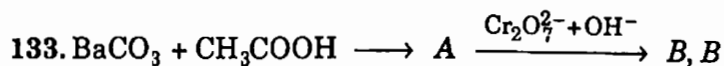
88. An orange colour mixture changes to green on acidification. Mixture may contain

- (a)  $\text{HgI}_2$ ,  $\text{CrO}_4^{2-}$
- (b)  $\text{Fe}^{2+}$ ,  $\text{C}_2\text{O}_7^{2-}$
- (c)  $\text{SO}_3^{2-}$ ,  $\text{MnO}_4^-$
- (d)  $\text{Fe}^{2+}$ ,  $\text{CrO}_4^{2-}$

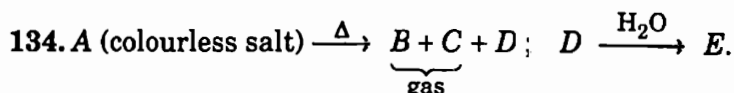
89. A colourless salt changes to yellow on heating. Salt is also soluble in NaOH as well as in dil. HCl. Salt can be  
 (a) FeO (b) PbO  
 (c) ZnO (d) CdO
90. A salt contains cation  $A^{2+}$  and anion  $B^{2-}$ . Both decolourise  $MnO_4^-$  in acidic medium. Salt is  
 (a) ferrous oxalate (b) ferric oxalate  
 (c) both (a) and (b) (d) None of these
91. A on reaction with dil.  $H_2SO_4$  gives a colourless pungent gas that can turn  $Cr_2O_7^{2-}/H^+$  green. Green colour is due to formation of  
 (a)  $CrO_4^{2-}$  (b)  $Cr^{3+}$   
 (c)  $CrO_3$  (d)  $CrO_2Cl_2$
92. Aqueous solution of A can dissolve AgBr forming a soluble complex B. A also reacts with aqueous  $AgNO_3$  solution giving white ppt. C changing to black ppt D. A, B, C and D are
- | A                | B                    | C            | D                    |
|------------------|----------------------|--------------|----------------------|
| (a) $Na_2S_2O_3$ | $Na_3[Ag(S_2O_3)_2]$ | $Ag_2S_2O_3$ | $Ag_2S$              |
| (b) $Na_2S_2O_3$ | $Ag_2S_2O_3$         | $Ag_2S$      | $Na_3[Ag(S_2O_3)_2]$ |
| (c) $NH_3$       | $[Ag(NH_3)_2]Br$     | $Ag(OH)$     | $Ag_2O$              |
| (d) $NH_3$       | $Na[Ag(OH)_2]$       | $Ag_2O$      | $[Ag(NH_3)_2]Br$     |
93.  $S^{2-}$  and  $SO_3^{2-}$  can be distinguished using  
 (a)  $(CH_3COO)_2Pb$  (b)  $Na_2[Fe(CN)_5NO]$   
 (c) both (a) and (b) (d) None of these
94. A mixture contains  $NO_2^-$  and  $SO_3^{2-}$ . On adding dilute  $H_2SO_4$  and KI and then starch, blue colour appears. This is due to  
 (a)  $NO_2^-$  (b)  $SO_3^{2-}$   
 (c) both (a) and (b) (d) None of these
95.  $SO_2$  can  
 (a) decolourise  $MnO_4^-/H^+$  solution  
 (b) turn  $Cr_2O_7^{2-}/H^+$  solution green  
 (c) both (a) and (b) are correct  
 (d) none of the above is correct
96. Cationic part of chromyl chloride is:  
 (a)  $Cr^{3+}$  (b)  $CrO_2^+$   
 (c)  $CrO_2^{2+}$  (d)  $CrO^{2+}$
97. Aqueous solution of a mixture contains  $Br^-$  and  $I^-$ . On passing  $Cl_2$  gas and adding  $CHCl_3$ , then organic layer will be  
 (a) violet (b) reddish brown  
 (c) colourless (d) blue
98.  $[Fe(H_2O)_5NO]^{2+}$  is formed as brown ring in  $NO_3^-$  test. Fe in this complex has ..... unpaired electrons.  
 (a) one (b) two  
 (c) three (d) four
99. A colourless salt gives white ppt with  $CaCl_2$  solution and can also decolourise  $MnO_4^-/H^+$ . Salt is decomposed by conc.  $H_2SO_4$  forming gases  
 (a)  $CO_2, SO_2$  (b)  $CO, CO_2$   
 (c)  $CO, SO_2$  (d)  $N_2, CO, CO_2$
100. Which is soluble in  $H_2O$ ?  
 (a) AgI (b) AgBr  
 (c) AgCl (d) AgF
101. Which is the volatile compound burning with green flame?  
 (a)  $(C_2H_5)_3B$  (b)  $(C_2H_5)_3BO_3$   
 (c)  $Ba(NO_3)_2$  (d)  $BaCl_2$
102. Test of this anion is not performed in glass test tubes. This anion is  
 (a)  $F^-$  (b)  $AsO_4^{3-}$   
 (c)  $PO_4^{3-}$  (d)  $BO_3^{3-}$
103. HF attacks glass ( $Na_2SiO_3$ ) forming  
 (a)  $Na_2SiF_6$  (b)  $Na_2SiF_3$   
 (c)  $Na_2SiF_6$  (d)  $H_4SiO_4$
104.  $SiF_4$  is hydrolysed by  $H_2O$  forming  
 (a)  $H_2SiF_6, H_4SiO_4$  (b)  $H_2SiF_4, H_2SiF_6$   
 (c)  $H_2SiF_6, H_2SiO_3$  (d)  $H_2SiF_6, SiO_2$
105. Water soluble mixture  $\xrightarrow[(ii) \text{ Filter}]{(i) BaCl_2}$  White ppt.  
 Filtrate +  $Br_2$  water +  $BaCl_2 \longrightarrow$  White ppt.  
 Mixture contains  
 (a)  $SO_3^{2-}$  only (b)  $SO_4^{2-}$  only  
 (c) both (a) and (b) (d) None of these
106. White ppt of AgCl and  $PbCl_2$  can be separated using  
 (a) aq  $NH_3$  (b) hot water  
 (c) both (a) and (b) (d) None of these
107. White ppt of A on reaction with aq  $NH_3$  are blackened. Select correct statement about A.  
 (a) A is also called calomel  
 (b) A reacts with aq  $NH_3$  forming  $HgNH_2Cl$   
 (c) A changes to grey on reaction with  $SnCl_2$   
 (d) all of the above are correct statements
108. Aqueous solution of A gives yellow ppt with aq  $K_2CrO_4$ . A may contain  
 (a)  $Pb^{2+}$  or  $Ag^+$  or  $Ba^{2+}$  (b)  $Pb^{2+}$  or  $Ba^{2+}$   
 (c)  $Ag^+$  or  $Ba^{2+}$  (d)  $Pb^{2+}$  or  $Ag^+$
109.  $Ag_2CrO_4$  (brick red ppt) is soluble in  
 (a) dil.  $HNO_3$  or aq.  $NH_3$  (b) dil. HCl or aq  $NH_3$   
 (c) dil.  $HNO_3$  or dil. HCl (d)  $H_2O$  or dil.  $HNO_3$
110.  $Ag_2CrO_4 + H^+NO_3^- \longrightarrow$  Soluble A, A is  
 (a)  $Ag_2CrO_4$  (b)  $AgNO_3$   
 (c)  $Ag_2Cr_2O_7$  (d)  $Ag_2O$
111.  $K_4[Fe(CN)_6]$  can be used to detect some ions out of  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Fe^{3+}$ ,  $Pb^{2+}$  and  $Bi^{3+}$ . Excluded ions are  
 (a)  $Fe^{3+}$ ,  $Bi^{3+}$ ,  $Pb^{2+}$  (b)  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Bi^{3+}$   
 (c)  $Bi^{3+}$ ,  $Pb^{2+}$  (d)  $Fe^{3+}$ ,  $Pb^{2+}$

12. Which gives ppt with  $K_2CrO_4$  ?  
 (a)  $Hg_2^{2+}$ ,  $Pb^{2+}$ ,  $Ag^+$ ,  $Ba^{2+}$  (b)  $Pb^{2+}$ ,  $Ag^+$ ,  $Ba^{2+}$   
 (c)  $Ag^+$ ,  $Ba^{2+}$  (d)  $Pb^{2+}$ ,  $Ba^{2+}$
13. Select correct statement.  
 (a)  $[Cu(CN)_4]^{3-}$  is more stable than  $[Cd(CN)_4]^{3-}$   
 (b) If  $H_2S$  gas is passed into the aqueous solution of mixture of  $[Cu(CN)_4]^{3-}$  and  $[Cd(CN)_4]^{3-}$ , formation of yellow ppt indicates presence of  $Cd^{2+}$   
 (c)  $HgI_2$  and  $BiI_3$  both dissolve in excess of  $KI$  forming soluble  $HgI_4^{2-}$  and  $BiI_4^-$ .  
 (d) All of the above are correct statements
14. Precipitates of IIA and IIB can be separated by  
 (a)  $NaOH$  (b) yellow  $(NH_4)_2S$   
 (c) both (a) and (b) (d) None of these
15. Eco-friendly reagent that can be used instead of  $H_2S$  is  
 (a)  $Na_2S$  (b)  $(NH_4)_2CS_3$   
 (c)  $(NH_4)_2S_2$  (d)  $S_8$
16.  $Fe^{3+}$  gives different colour with  
 (a)  $CNS^-$  (b)  $[Fe(CN)_6]^{4-}$   
 (c)  $CH_3COO^-$  (d) all of these
17.  $Fe(OH)_3$  and  $Cr(OH)_3$  can be separated using  
 (a)  $NaOH$  (b)  $NaOH + H_2O_2$   
 (c) both (a) and (b) (d) None of these
18.  $Fe(OH)_3$  and  $Al(OH)_3$  can be separated using  
 (a)  $NaOH$  (b)  $KOH + Br_2$  water  
 (c) both (a) and (b) (d) None of these
19. Select correct statement.  
 (a) Prussian blue and Turnbull's blue are identical in structure  
 (b)  $NH_4Cl$  decreases ionisation of  $NH_4OH$  by common ion effect so as to precipitate only  $Al^{3+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$  as hydroxides.  
 (c) Both (a) and (b) are correct  
 (d) None of the above is correct
20. By  $H_2O_2/OH^-$ ,  $Cr(OH)_3$  changes to  
 (a)  $CrO_3$  (b)  $Cr_2O_7^{2-}$   
 (c)  $CrO_4^{2-}$  (d)  $[Cr(OH)_4]^-$
21. On adding  $KNO_2$  and  $CH_3COOH$  solution to the neutral solution of  $CoCl_2$ , there is formation of yellowish orange precipitate of  
 (a)  $K_3[Co(NO_2)_6]$   
 (b)  $K_4[Co(NO_2)_6]$   
 (c)  $K_3[Co(NO_2)_4(CH_3COO)_2]$   
 (d)  $K_2[Co(NO_2)_4]$
22. Which set does not contain amphoteric species?  
 (a)  $Al(OH)_3$ ,  $Zn(OH)_2$  (b)  $SnO_2$ ,  $Al_2O_3$   
 (c)  $Fe(OH)_3$ ,  $Ni(OH)_2$  (d) All of these
23.  $PbO_2$  oxidises  $MnO_2$  (black) to  
 (a)  $MnO_4^{2-}$  (b)  $MnO_4^-$   
 (c)  $Mn^{2+}$  (d)  $Mn_2O_7$
24. Test tube A contains  $ZnCl_2$  aqueous solution while test tube B contains aq  $CdCl_2$  solution. On passing  $H_2S$  gas  
 (a)  $ZnS$  is precipitated  
 (b)  $CdS$  is precipitated  
 (c) both (a) and (b) are precipitated  
 (d) None of the above is precipitated
25. Dimethyl glyoxime and  $NaHSO_3/NH_4CNS$  are used to distinguish and separate  $Cu^{2+}$  and  $Ni^{2+}$ . These are used in order  
 (a)  $HSO_3^-/CNS^-$  then DMG  
 (b) DMG then  $HSO_3^-/CNS^-$   
 (c) at random  
 (d) given reagents are not suitable
26. Which cation cannot be identified by flame test?  
 (a)  $Na^+$  (b)  $K^+$   
 (c)  $Ba^{2+}$  (d)  $Mg^{2+}$
27. When microcosmic salt is heated, transparent bead is of  
 (a)  $NaPO_3$  (b)  $Na(NH_4)HPO_4$   
 (c)  $NaBO_2$  (d)  $B_2O_3$
28. In borax-bead test there is formation of transparent bead of  
 (a)  $NaPO_3$  and  $NaBO_2$   
 (b)  $NaBO_2$  and  $Na_2B_4O_7$   
 (c)  $NaBO_2$  and  $B_2O_3$   
 (d)  $NaPO_3$  and  $B_2O_3$
29. In sodium carbonate bead test, chromium salts (green) change to coloured bead  
 (a) yellow,  $PbCrO_4$  (b) yellow,  $BaCrO_4$   
 (c) yellow,  $Na_2CrO_4$  (d) orange,  $Na_2Cr_2O_7$
30. Microcosmic salt and borax are used in the identification of cations by dry tests. They are respectively  
 (a)  $NaBO_2$  and  $NaPO_3$   
 (b)  $NaNH_4HPO_4 \cdot 4H_2O$  and  $Na_2B_4O_7 \cdot 10H_2O$   
 (c)  $NaPO_3$  and  $NaBO_2$   
 (d)  $Na_2B_4O_7$  and  $NaNH_4HPO_4$
31. Which is not soluble in  $CH_3COOH$  ?  
 (a)  $CaC_2O_4$  (b)  $Na_2C_2O_4$   
 (c)  $K_2C_2O_4$  (d)  $CaCO_3$
32. Acidified  $MnO_4^-$  can be decolourised by  
 (a)  $CaC_2O_4$  (b)  $H_2O_2$   
 (c)  $FeSO_4$  (d) all of these





- (a)  $\text{BaCr}_2\text{O}_7$  (b)  $\text{BaCrO}_4$   
(c)  $\text{BaCrO}_3$  (d)  $\text{Ba}_2\text{Cr}_2\text{O}_4$

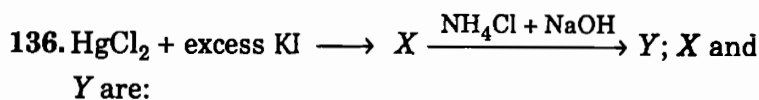


Gas C turns solution E milky. B burns with blue flame. A also decolourises  $\text{MnO}_4^-/\text{H}^+$ . Thus, A, B, C, D and E are

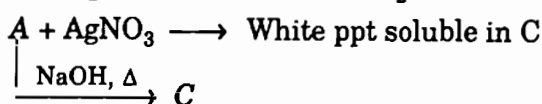
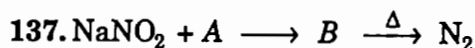
| A                            | B             | C             | D             | E                 |
|------------------------------|---------------|---------------|---------------|-------------------|
| (a) $\text{CaC}_2\text{O}_4$ | CO            | $\text{CO}_2$ | CaO           | $\text{Ca(OH)}_2$ |
| (b) $\text{CaC}_2\text{O}_4$ | $\text{CO}_2$ | CO            | CaO           | $\text{Ca(OH)}_2$ |
| (c) $\text{CaCO}_3$          | CaO           | CO            | $\text{CO}_2$ | $\text{Ca(OH)}_2$ |
| (d) $\text{CaOCl}_2$         | $\text{Cl}_2$ | $\text{O}_2$  | CaO           | $\text{Ca(OH)}_2$ |

135. Metal chloride A is soluble in hot water but insoluble in cold water. Select correct statement about A. Thus

- (a) A can give yellow ppt. with  $\text{K}_2\text{CrO}_4$   
(b) A can give white ppt with  $\text{K}_2\text{SO}_4$   
(c) A can give yellow ppt with KI  
(d) all the above are correct statements



| X                            | Y                                                                                  |
|------------------------------|------------------------------------------------------------------------------------|
| (a) $\text{HgI}_2$           | $\text{NH}_4\text{I}$                                                              |
| (b) $\text{K}_2\text{HgI}_4$ | $(\text{NH}_4)_2\text{HgI}_4$                                                      |
| (c) $\text{K}_2\text{HgI}_4$ | $\text{O} \begin{array}{c} \text{Hg} \\ \text{Hg} \end{array} \text{NH}_2\text{I}$ |
| (d) $\text{HgI}_2$           | $\text{O} \begin{array}{c} \text{Hg} \\ \text{Hg} \end{array} \text{NH}_2\text{I}$ |



Hence, A is

- (a) NaCl (b)  $\text{NH}_4\text{Cl}$   
(c)  $\text{NH}_4\text{NO}_2$  (d)  $\text{NH}_4\text{NO}_3$

138.  $A \longrightarrow B(\text{gas})$  used by dentist. Hence, A is

- (a)  $\text{NH}_4\text{Cl}$  (b)  $\text{NH}_4\text{NO}_2$   
(c)  $\text{NH}_4\text{NO}_3$  (d)  $\text{NH}_4\text{OH}$

139. Reagent that can detect presence of  $\text{NH}_3$  is called

- (a) Fehling's solution  
(b) Nessler's reagent  
(c) Benedict's solution  
(d) Lucas reagent

140. Ammonium salts can be decomposed by

- (a) aq  $\text{Na}_2\text{O}$  (b) aq CaO  
(c) both (a) and (b) (d) None of these

## One or More Than One Options Correct

1.  $\text{K}_4[\text{Fe(CN)}_6]$  can be used to test

- (a)  $\text{Fe}^{3+}$  (b)  $\text{Fe}^{2+}$   
(c)  $\text{Zn}^{2+}$  (d)  $\text{Cd}^{2+}$

2. NaOH can dissolve

- (a)  $\text{Cr(OH)}_3$  (b)  $\text{Al(OH)}_3$   
(c)  $\text{Zn(OH)}_2$  (d)  $\text{Fe(OH)}_3$

3.  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  ions are precipitated together by addition of

- (a) aq.  $\text{NH}_3$  (b)  $\text{K}_2\text{C}_2\text{O}_4$  solution  
(c) dil.  $\text{HNO}_3$  (d) KI solution

4. An inorganic mixture gives yellow precipitate on boiling with conc.  $\text{HNO}_3$  and ammonium molybdate  $(\text{NH}_4)_2\text{MoO}_4$ . Thus, inorganic mixture can be

- (a)  $(\text{NH}_4)_3\text{PO}_4$  (b)  $(\text{NH}_4)_3\text{AsO}_4$   
(c)  $\text{Pb(NO}_3)_2$  (d)  $(\text{NH}_4)_2\text{C}_2\text{O}_4$

5. KCN is used in the

- (a) separation of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$   
(b) metallurgical extraction of  $\text{Ag}^+$  and  $\text{Au}^+$   
(c) identification of  $\text{Fe}^{3+}$   
(d) treatment of cancer

6. Precipitation of cations as sulphide can be done by

- (a)  $\text{H}_2\text{S}$  (b) CdS  
(c)  $\text{K}_2\text{CS}_3$  (d)  $(\text{NH}_4)_2\text{S}_2$

7. Borax-bead test can be used to identify following ions

- (a)  $\text{Ca}^{2+}$  (b)  $\text{Cr}^{3+}$   
(c)  $\text{Mn}^{2+}$  (d)  $\text{Cu}^{2+}$

8. Zinc oxalate can be tested by

- (a) NaOH when white precipitate is formed which dissolves in excess of NaOH  
(b)  $\text{KMnO}_4$  which is decolourised  
(c)  $\text{CaCl}_2$  which gives white precipitate  
(d)  $\text{K}_4[\text{Fe(CN)}_6]$  which gives yellowish white precipitate

9. Select correct statement(s).

- (a) CdS and  $\text{As}_2\text{S}_3$  can be separated using NaOH or yellow ammonium sulphide  
(b)  $\text{FeCl}_3$  gives blue precipitate with  $\text{K}_4[\text{Fe(CN)}_6]$   
(c)  $\text{FeCl}_3$  gives blood red colour with KCNS  
(d) Aq  $\text{FeCl}_3$  is reduced to  $\text{FeCl}_2$  when Zn pieces are added

10. Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution changes to green

- (a) when  $\text{SO}_2$  gas is passed into it  
(b) when  $\text{FeCl}_3$  is added to it  
(c) when  $\text{FeSO}_4$  is added to it  
(d) when  $\text{H}_2\text{O}_2$  is added to it

## Brain Twisters

1. (A) is hydrated salt. 2.48 g of (A) on heating gives 1.58 g of anhydrous salt (B).

- (i) Aqueous (A) +  $\text{AgNO}_3 \longrightarrow$  white turbidity changing to black.  
 (ii) Aqueous (A) decolourises  $\text{I}_2$  in KI  
 (iii) Aqueous (A) + dil.  $\text{HCl} \longrightarrow$  white turbidity.  
 (iv) Aqueous (A) dissolves unreacted  $\text{AgBr}$  of photographic plate.

Identify (A) and explain reactions.

2. When a substance (A) was treated with dil.  $\text{HCl}$ , a colourless gas (B) was evolved, which turned moist litmus paper red. On bubbling (B) thorough lime water, a precipitate (C) was formed, but passage of further gas resulted in a clear solution (D). A small sample of (A) was moistened with conc.  $\text{HCl}$  and placed on a platinum wire, and introduced in to a Bunsen burner flame where it caused a green flame colouration. On strong heating, (A) decomposed, giving a white solid (E) which turned red litmus paper blue. 1.9735 g of (A) was heated strongly and gave 1.5334 g of (E). The sample (E) was dissolved in water and made upto 250 mL in a standard flask. 25 mL aliquots were titrated with acid and required 20.30 mL of 0.0985 M  $\text{HCl}$ . Name the compounds (A) to (E), and give equations for all the reactions. Calculate the gram molecular weight of (A).

3. Identify (A) to (O) in the following (A) (hydrated bluish brown coloured double salt) gives white ppt (B) with  $\text{BaCl}_2$  insoluble in conc.  $\text{HCl}$ . 0.9915 g of (A) gave 0.932 g of white ppt.

(A) (in dil.  $\text{HCl}$ )  $\xrightarrow{\text{H}_2\text{S}}$  black ppt (C)

(insoluble in yellow ammonium sulphide)

blue ppt (E)  $\xleftarrow{\text{aq. NH}_3}$  blue coloured solution (D)  
 $\downarrow$  excess aq.  $\text{NH}_3$   $\downarrow$  KI  $\downarrow$   $\text{NH}_4\text{SCN}$   
 deep blue white ppt (G) black ppt (H)  
 solution (F) (appeared after adding hypo)

Filtrate after separating (C)  $\xrightarrow{\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}}$  brown ppt (I)

light green coloured  $\xleftarrow{\text{Gas (K)}}$  yellow coloured  $\xleftarrow{\text{HCl}}$   
 solution (L) solution (J)

blue (M)  $\xleftarrow{\text{K}_4[\text{Fe}(\text{CN})_6]}$   $\downarrow$   $\text{SnCl}_2$   $\rightarrow$  green (L)  
 $\downarrow$   $\text{NH}_4\text{SCN}$   
 $\text{K}_3[\text{Fe}(\text{CN})_6] \rightarrow$  blue (O) intense red (N)

(Cu = 63.5, Fe = 56,  $\text{SO}_4^{2-}$  = 96,  $\text{H}_2\text{O}$  = 18,  $\text{Ba}^{2+}$  = 137)

4. (A) is binary orange coloured paramagnetic compound of a univalent cation. 1.422 g of (A) reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid (B) that forms hydrated double salt (C) with  $\text{Al}_2(\text{SO}_4)_3$ ; what are (A), (B) and (C) and explain reactions?

5. Hydrated salt (A) +  $\text{BaCl}_2 \longrightarrow$  white ppt (B) insoluble in  $\text{HNO}_3$ .

(A) (in dil.  $\text{HCl}$ ) +  $\text{H}_2\text{S} \longrightarrow$  black ppt soluble in 50%  $\text{HNO}_3$

(A) + aq  $\text{NH}_3$  (excess)  $\longrightarrow$  deep blue solution (C)

(A) + microcosmic salt  $\xrightarrow{\Delta}$  green (D) when hot

(A) + KI solution  $\longrightarrow$  reddish brown changing to white ppt after hypo is added.

2.495 g of (A) gave 2.33 g of (B). Identify (A), (B), (C) and (D) and explain reactions.

6. 0.347 g of a metal (A) was dissolved in dil.  $\text{HNO}_3$ . This solution gave a red colouration to a non-luminous Bunsen burner flame, and on evaporation gave 0.747 g of metal oxide (B). (A) also reacted with nitrogen, forming a compound (C), and with hydrogen, forming (D). On reacting 0.1590 g of (D) with  $\text{H}_2\text{O}$ , a gas (E) was evolved and a sparingly soluble compound (F) formed, which gave a strongly basic reaction and required 200 mL of 0.1 M  $\text{HCl}$  to neutralise it. Identify the substances (A) to (F) and explain the reactions involved.

7. Identify inorganic salt (A) which is hydrated and light green in colour and gives following reactions

(i) (A) decolourises acidified  $\text{MnO}_4^-$  and turns acidified  $\text{Cr}_2\text{O}_7^{2-}$  green.

(ii) (A) in aqueous solution gives light green turbidity which dissolves in dil. acid.

(iii) (A) gives white ppt with  $\text{BaCl}_2$  solution insoluble in conc.  $\text{HCl}$ . 2.78 g of (A) gave 2.33 g of white ppt.

(iv) (A)  $\xrightarrow{\Delta}$  (B) + (C) + (D)  
 (blackish brown) oxides of sulphur

(C)  $\xrightarrow{\text{oxidation}}$  (D)

(C) turns acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution green

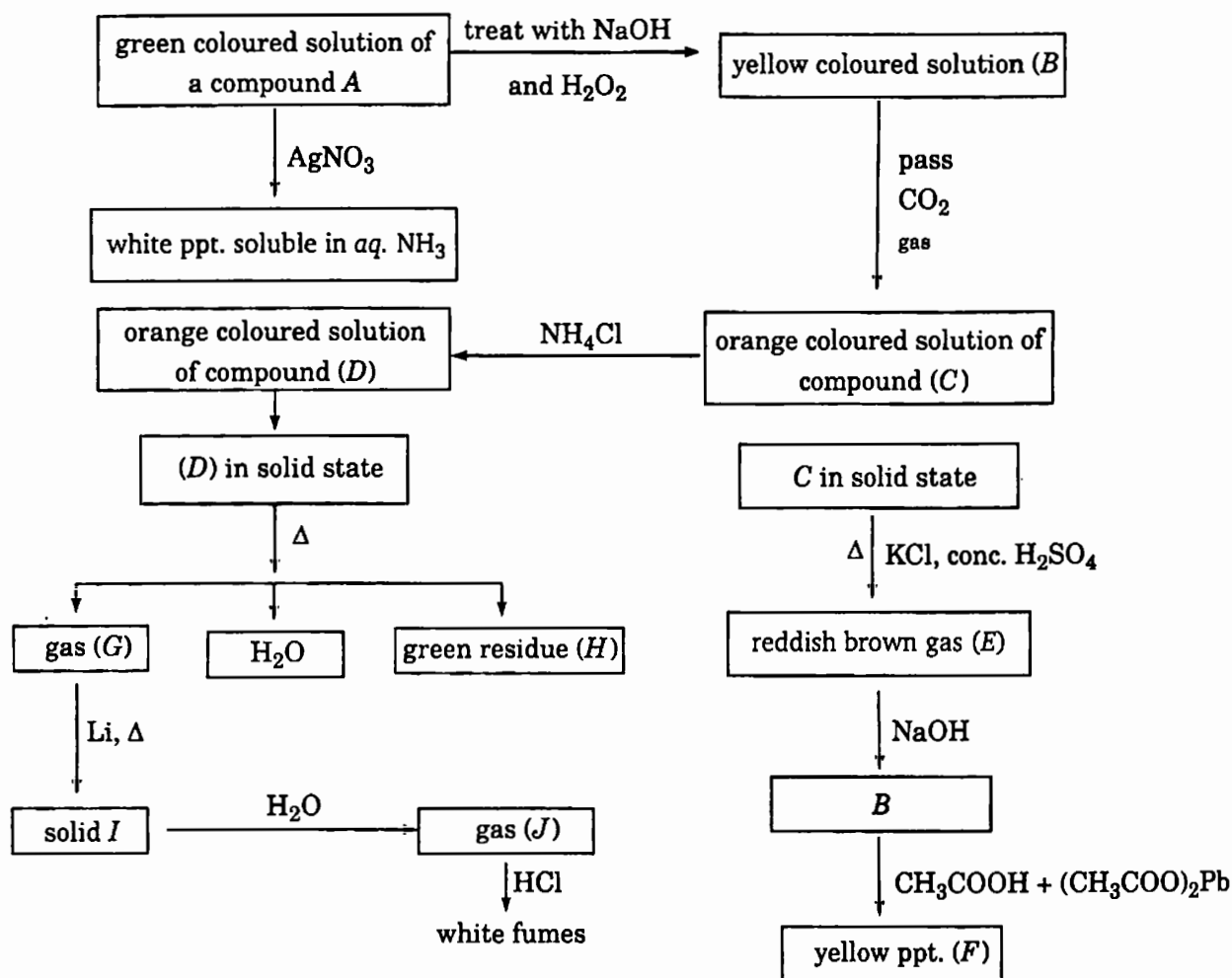
(B) +  $\text{HCl} \xrightarrow{\Delta}$  (E)  
 deep yellow

(E) +  $\text{KCNS} \longrightarrow$  red colour

## Passage Comprehension Questions

## Passage 1

Following flow sheet has been given to analyse a salt. Based on the various stages, answer the questions at the end of it.



- Compound (A) is
  - $\text{CuCl}_2$
  - $\text{FeCl}_3$
  - $\text{FeCl}_2$
  - $\text{CrCl}_3$
- Yellow coloured solution (B) is of
  - $\text{Na}_2\text{CrO}_4$  formed by oxidation of  $\text{Cr}^{3+}$  by  $\text{H}_2\text{O}_2$  in alkaline medium
  - $\text{FeCl}_2$  formed by reduction of  $\text{FeCl}_3$  by  $\text{H}_2\text{O}_2$
  - $\text{FeCl}_3$  formed by oxidation of  $\text{FeCl}_2$  by  $\text{H}_2\text{O}_2$
  - $\text{Cu}(\text{OH})_2$  formed by precipitation of  $\text{CuCl}_2$  by  $\text{H}_2\text{O}_2/\text{NaOH}$
- Select correct statement(s).
  - $\text{CO}_2$  makes the solution of (B) acidic and converts (B) into  $\text{FeCl}_2$  (C)
  - $\text{CO}_2$  makes the solution of (B) basic and converts it into  $\text{Na}_2\text{Cr}_2\text{O}_7$
  - $\text{CO}_2$  makes the solution of (B) acidic and converts it into  $\text{Na}_2\text{Cr}_2\text{O}_7$
  - None of the above is correct
- Formation of (F) using (G), KCl and conc.  $\text{H}_2\text{SO}_4$  is called
  - redox test of  $\text{Cr}_2\text{O}_7^{2-}$
  - chromyl-chloride test of  $\text{Cl}^-$
  - chromyl-chloride test of  $\text{Cr}^{3+}$
  - none of the above is correct
- Compounds D, E and F respectively are
 

| D                                          | E                         | F                |
|--------------------------------------------|---------------------------|------------------|
| (a) $(\text{NH}_4)_2\text{CrO}_4$          | $\text{CrO}_2\text{Cl}_2$ | $\text{PbCrO}_4$ |
| (b) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ | $\text{CrO}_3$            | $\text{PbCrO}_4$ |
| (c) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ | $\text{CrO}_2\text{Cl}_2$ | $\text{PbCrO}_4$ |
| (d) $(\text{NH}_4)_2\text{CrO}_4$          | $\text{CrO}_3$            | $\text{PbCrO}_4$ |
- Compounds G, H, I and J are respectively
 

| G                | H                       | I                     | J             |
|------------------|-------------------------|-----------------------|---------------|
| (a) $\text{N}_2$ | $\text{CrO}_3$          | $\text{Li}_3\text{N}$ | $\text{NH}_3$ |
| (b) $\text{O}_2$ | $\text{CrO}_3$          | $\text{Li}_2\text{O}$ | $\text{H}_2$  |
| (c) $\text{O}_2$ | $\text{Cr}_2\text{O}_3$ | $\text{Li}_2\text{O}$ | $\text{O}_2$  |
| (d) $\text{N}_2$ | $\text{Cr}_2\text{O}_3$ | $\text{Li}_3\text{N}$ | $\text{NH}_3$ |

### Passage 2

Silver nitrate gives a white precipitate (A) with aqueous sodium thiosulphate (B); the precipitate dissolves in excess of thiosulphate. If the precipitate is heated with water, it turns black (C), and the supernatant liquid then gives a white precipitate (D) with acidified barium nitrate solution.

Read the above analysis-report and answer the questions given below:

1. Species A and B are respectively

| A                                            | B                                        |
|----------------------------------------------|------------------------------------------|
| (a) $\text{Ag}_2\text{S}_2\text{O}_3$        | $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ |
| (b) $\text{AgS}_2\text{O}_3$                 | $\text{Ag}(\text{S}_2\text{O}_3)_2^{2-}$ |
| (c) $\text{AgS}_2\text{O}_3$                 | $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ |
| (d) $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ | $\text{Ag}_2\text{S}_2\text{O}_3$        |

2. Select correct explanation for the formation of C and D

- (a) When (B) is heated with  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$  is formed which gives black ppt of  $\text{Ag}_2\text{S}$ .  
 (b)  $\text{Ag}_2\text{S}$  (black C) is precipitated alongwith  $\text{H}_2\text{SO}_4$  (in supernatant layer) which gives white ppt with  $\text{Ba}(\text{NO}_3)_2$  solution  
 (c)  $\text{Ag}_2\text{SO}_4$  (black C) is precipitated alongwith  $\text{H}_2\text{S}$  which gives white ppt with  $\text{Ba}(\text{NO}_3)_2$  solution  
 (d) None of the above is correct explanation

### Passage 3

Questions given below are based on the following analysis.

A coloured solution known to contain two metal ions, was treated with excess cold sodium hydroxide solution. When filtered a whitish solid, slowly changing to brown, was retained on the filter paper and a colourless solution collected as the filtrate. Dropwise addition of hydrochloric acid to the filtrate produced a white precipitate which dissolved in excess acid. Treatment of the residue from the filter paper with a solution of a strong oxidiser produced a reddish-violet solution.

1. Indicate any pairs of ions which on testing as above leads to the observed changes

- (a)  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  ions    (b)  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$  ions  
 (c)  $\text{Mn}^{2+}$  and  $\text{Mg}^{2+}$  ions    (d)  $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$  ions

2. Filtrate obtained after separation of white solid contains

- (a)  $\text{ZnO}$     (b)  $\text{Na}_2\text{ZnO}_2$   
 (c)  $\text{MnO}$     (d)  $\text{Na}_2\text{MnO}_2$

3. White solid changing to brown is due to formation of

- (a)  $\text{Mn}(\text{OH})_2$     (b)  $\text{MgO}$   
 (c)  $\text{Zn}(\text{OH})_2$     (d)  $\text{MnO}_2$

4. Reddish-violet solution obtained by oxidation is of

- (a)  $\text{ZnO}_2^{2-}$     (b)  $\text{MnO}_4^{2-}$   
 (c)  $\text{MnO}_4^-$     (d)  $\text{MnO}_2$

5. Reddish-violet solution is decolourised by  
 (a)  $\text{SO}_3^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{Fe}^{2+}$     (b)  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{Fe}^{3+}$   
 (c)  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Fe}^{2+}$     (d)  $\text{H}_2\text{O}_2$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{CO}_3^{2-}$

### Passage 4

You have a mixture of  $\text{CO}_2$ ,  $\text{SO}_2$  and  $\text{O}_2$  gas. You have been provided following reagents for testing

- (A) lime water  
 (B) acidified potassium dichromate solution  
 (C) pyrogallol

1. Arrange these reagents in order such that only one gas is tested at one time

- (a) A, B, C    (b) B, C, A  
 (c) B, A, C    (d) A, C, B

2. If order is A, B, C, then which gas remains unchecked

- (a)  $\text{CO}_2$     (b)  $\text{SO}_2$   
 (c)  $\text{O}_2$     (d) none of these

3. Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution has been used to test

- (a)  $\text{SO}_2$   
 (b)  $\text{CO}_2$   
 (c)  $\text{O}_2$   
 (d) mixture of  $\text{SO}_2$  and  $\text{CO}_2$

4. Gas responsible for green-house effect is

- (a)  $\text{O}_2$     (b)  $\text{SO}_2$   
 (c)  $\text{CO}_2$     (d)  $\text{CO}_2$  and  $\text{O}_2$

### Passage 5

A colourless mixture of two salts (A) and (B) (excess) is soluble in  $\text{H}_2\text{O}$ . Separately (A) turns blue litmus red and (B) turns red litmus blue. (A) gives white ppt. with (B), which dissolves in excess of (B) forming (C). (A) when placed in moist air gives fumes and can form dimer. (A) gives white ppt. with  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  soluble in (B). A also gives white ppt. with  $\text{AgNO}_3$  soluble in  $\text{NH}_4\text{OH}$ .

Read the above analysis report and answer the following questions:

1. Colourless mixture contains

- (a)  $\text{ZnCl}_2$ ,  $\text{NaOH}$     (b)  $\text{AlCl}_3$ ,  $\text{NaCl}$   
 (c)  $\text{AlCl}_3$ ,  $\text{NaOH}$     (d)  $\text{CrCl}_3$ ,  $\text{NaOH}$

2. A remains soluble in  $\text{H}_2\text{O}$  in presence of excess of B. It is due to formation of

- (a)  $\text{Na}_2\text{Zn}(\text{OH})_2$     (b)  $\text{NaAl}(\text{OH})_4$   
 (c)  $\text{Na}_2\text{Zn}(\text{OH})_4$     (d)  $\text{Al}_2\text{O}_3$

3. A turns blue litmus red. It is due to acidic solution because of

- (a) hydrolysis of cation of A  
 (b) hydrolysis of anion of A  
 (c) hydrolysis of both cation and anion  
 (d) none of the above is correct

4. White fumes are formed in moist air. It is due to formation of

- (a)  $\text{Al}(\text{OH})_3$     (b)  $\text{HCl}$   
 (c)  $\text{Zn}(\text{OH})_2$     (d)  $\text{NaAlO}_2$

5. Dimer formed has bonding  
 (a) ionic, covalent (b) ionic, coordinate  
 (c) covalent (d) covalent, coordinate
6.  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  acts as a buffer for precipitation of A as white ppt. If  $\text{p}K_b$  of  $\text{NH}_3(\text{aq})$  is 4.74, pH of equimolar  $[\text{NH}_4^+]$  and  $[\text{NH}_3]$  will be  
 (a) 4.74 (b) 9.26  
 (c) 7.00 (d) 14.00
7. If ppt. formed by addition of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  is of the form  $M(\text{OH})_3$  then pH at which  $2 \times 10^{-12} \text{ M } M^{3+}$  ion is precipitated is ( $K_{sp}$  of  $M(\text{OH})_3 = 2 \times 10^{-33}$ )  
 (a) 7 (b) 5  
 (c) 6 (d) 8

### Passage 6

Presence of  $\text{Fe}^{3+}$  in an aqueous solution can be made by addition of sodium acetate (in excess) when a reddish-brown colour is formed".

Read the above short write-up and answer the following questions:

- Reddish-brown colour is due to formation of  
 (a)  $[\text{Fe}(\text{H}_2\text{O})_4(\text{CH}_3\text{COO})_2]^+$   
 (b)  $[\text{Fe}(\text{CH}_3\text{CO}_4)_6]^{3-}$   
 (c)  $[\text{Fe}_3(\text{OH})_2(\text{CH}_3\text{COO})_6]^+$   
 (d)  $[\text{Fe}_2(\text{H}_2\text{O})_4(\text{CH}_3\text{COO})_4]^{2+}$
- Excess of sodium acetate is added in the above test. It is because  
 (a) it acts as a buffer to control pH of the reaction otherwise reaction is made reversible  
 (b) it makes the solution alkaline which destroys acidic effect if any  
 (c) sodium acetate has low  $K_{sp}$  value  
 (d) sodium acetate has high  $K_{sp}$  values
- Presence of  $\text{Fe}^{3+}$  can also be detected by ..... when ..... is formed.  
 (a)  $\text{KCNS}$ ,  $\text{Fe}(\text{CNS})_3$  ... blood red  
 (b)  $\text{KCNS}$ ,  $[\text{Fe}(\text{CNS})]\text{Cl}_2$  ... blood red colour  
 (c)  $\text{KCNS}$ ,  $[\text{Fe}(\text{CNS})_2\text{Cl}]$  ... blood red colour  
 (d)  $\text{KCN}$ ,  $\text{K}_3[\text{Fe}(\text{CN})_6]$  ... blue precipitate
- A blue colour solution is formed when potassium ferrocyanide in excess is added to aqueous ferric chloride solution. This blue colour is of  
 (a)  $\text{KFe}[\text{Fe}(\text{CN})_6]$  or  $\text{KFe}[\text{Fe}(\text{CN})_6]$   
 (b)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$   
 (c)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$   
 (d) None of the above

### Passage 7

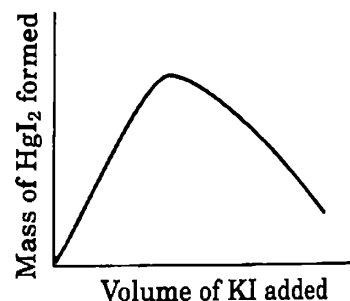
"Sometimes it happens that when  $\text{H}_2\text{S}$  gas is passed into a solution in dil.  $\text{HCl}$  (in qualitative analysis of cations), yellowish white turbidity appears."

Read the above short write-up and answer the following questions:

- Yellowish white turbidity is of  
 (a)  $\text{SO}_3^{2-}$  formed by oxidation of  $\text{H}_2\text{S}$  by  $\text{HCl}$   
 (b) colloidal sulphur formed by oxidation of  $\text{H}_2\text{S}$  by certain oxidising agent  
 (c)  $\text{SO}_4^{2-}$  formed by oxidation of  $\text{H}_2\text{S}$  by  $\text{H}_2\text{O}$   
 (d) None of the above is correct
- A colourless salt on reaction with dil.  $\text{HCl}$  gives a colourless pungent gas that turns  $\text{K}_2\text{Cr}_2\text{O}_7$  solution green. A student passed  $\text{H}_2\text{S}$  gas immediately after adding dil.  $\text{HCl}$  and got colloidal yellowish suspension before any precipitation occurs. This is due to:  
 (a)  $\text{SO}_3^{2-}$  which is decomposed to  $\text{SO}_2$  forming S with  $\text{H}_2\text{S}$   
 (b)  $\text{NO}_2^-$  which oxidises  $\text{H}_2\text{S}$  to colloidal sulphur  
 (c) both of the above  
 (d) none of the above

### Passage 8

When a  $\text{KI}$  solution was added to a solution of mercury (II) chloride, a precipitate [mercury (II) iodide] formed. A student plotted the mass of the precipitate *versus* the volume of the  $\text{KI}$  solution added and obtained the following graph.



Based on the above graph, answer the following questions:

- As  $\text{KI}$  is added to  $\text{HgCl}_2$  solution, there is increase in the mass of  $\text{HgI}_2$  but after a maximum point is reached, mass of  $\text{HgI}_2$  decreases. It is due to  
 (a) formation of soluble  $\text{K}_3\text{HgI}_5$   
 (b) formation of soluble  $\text{K}_2\text{HgI}_4$   
 (c) decomposition of  $\text{HgI}_2$  into  $\text{Hg}_2\text{I}_2$  and  $\text{I}_2$   
 (d) decomposition of  $\text{HgI}_2$  into  $\text{Hg}$  and  $\text{I}_2$
- Species formed after maximum is attained is called  
 (a) Nessler's reagent  
 (b) Tollen's reagent  
 (c) iodide of Millon's base  
 (d) none of the above is correct
- (Refer Q. 2). Species formed in Q. 2 is added to hot  $\text{NH}_4\text{Cl}$  solution containing some  $\text{NaOH}$ , then there is formation of  
 (a) brown precipitate of iodide Millon's base  
 (b) yellow colouration of  $\text{K}_2\text{HgI}_4$   
 (c) blue precipitate of  $(\text{NH}_4)_2\text{HgI}_2\text{Cl}_2$   
 (d) none of the above

## Assertion & Reason

### Codes

- (a) Both **A** and **R** are true and **R** is the correct explanation of **A**.  
 (b) Both **A** and **R** are true but **R** is not the correct explanation of **A**.  
 (c) **A** is true but **R** is false.  
 (d) **A** is false but **R** is true.  
 (e) **A** and **R** both are false.

1. **Assertion (A)** : When  $\text{H}_2\text{S}(g)$  is passed into aqueous  $\text{ZnCl}_2$  solution,  $\text{ZnS}$  is precipitated.

**Reason (R)** :  $\text{ZnS}$  is insoluble in dil.  $\text{HCl}$ .

2. **Assertion (A)** : When  $\text{H}_2\text{S}(g)$  is passed into aqueous  $\text{Zn}(\text{CH}_3\text{COO})_2$  solution, zinc is precipitated as  $\text{ZnS}$ .

**Reason (R)** :  $\text{CH}_3\text{COOH}$  is produced in the reaction which cannot dissolve  $\text{ZnS}$  formed.

3. **Assertion (A)** :  $\text{PbCl}_2$  and  $\text{Hg}_2\text{Cl}_2$  precipitates can be separated by hot water.

**Reason (R)** :  $\text{Hg}_2\text{Cl}_2$  is blackened by *aq.*  $\text{NH}_3$ .

4. **Assertion (A)** :  $\text{PbCl}_2$  and  $\text{AgCl}$  precipitates can be separated by *aq.*  $\text{NH}_3$ .

**Reason (R)** :  $\text{PbCl}_2$  precipitates change to soluble complex  $[\text{Pb}(\text{NH}_3)_4]\text{Cl}_2$ .

5. **Assertion (A)** : Basic radicals (cations) have been divided into groups based on  $K_{sp}$  values.

**Reason (R)** : Mostly alkali salts are water soluble.

6. **Assertion (A)** :  $\text{NO}_2^-$  is decomposed by urea in the mixture of  $\text{NO}_3^-$  and  $\text{NO}_2^-$ .

**Reason (R)** :  $\text{NO}_3^-$  interferes in the ring test of  $\text{NO}_2^-$ .

7. **Assertion (A)** :  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  solution is complexed by addition of  $\text{KCNS}$ .

**Reason (R)** : On passing  $\text{H}_2\text{S}$  gas stable complex  $[\text{Cu}(\text{CN})_4]^{3-}$  is not affected.

8. **Assertion (A)** :  $\text{CO}_2$  containing  $\text{H}_2\text{O}$  changes yellow  $\text{CrO}_4^{2-}$  into  $\text{Cr}_2\text{O}_7^{2-}$ .

**Reason (R)** : Aqueous  $\text{CO}_2$  is acidic ( $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ ) which converts  $\text{CrO}_4^{2-}$  into  $\text{Cr}_2\text{O}_7^{2-}$ .

9. **Assertion (A)** : Unreacted  $\text{AgNO}_3$  of photographic plate is removed by  $\text{Na}_2\text{S}_2\text{O}_3$  (hypo).

**Reason (R)** :  $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$  is soluble complex.

10. **Assertion (A)** : Coloured cations can be identified by borax-bead test.

**Reason (R)** : Transparent bead ( $\text{NaBO}_2 + \text{B}_2\text{O}_3$ ) forms coloured bead with coloured cation.

2. Dilute  $\text{H}_2\text{SO}_4$  can be used instead of dil.  $\text{HCl}$  in group II.

3. When  $\text{H}_2\text{S}$  gas is passed into *aq.*  $\text{ZnCl}_2$  solution, white ppt of  $\text{ZnS}$  is obtained.

4. When  $\text{Cl}_2$  gas is passed into a mixture containing  $\text{Br}^-$  and  $\text{I}^-$  and  $\text{CHCl}_3$ ,  $\text{I}_2$  (violet) first appears in  $\text{CHCl}_3$  layer.

5. There is precipitation of solute  $AB$  if its ionic product is greater than  $K_{sp}$  value, i.e.,  $[A][B] > K_{sp}$ .

6. If  $K_{sp}$  of  $M(\text{OH})_3$  is  $1 \times 10^{-12}$  then 0.001 M.  $M^{3+}$  is precipitated at a  $\text{pH} > 9$ .

7. Turnbull's blue and Prussian's blue respectively are  $\text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ ,  $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$

8.  $\text{BaBr}_2$  gives yellow ppt. with  $\text{AgNO}_3$  as well as with  $\text{K}_2\text{CrO}_4$ .

9.  $\text{AlCl}_3$  is soluble in excess of  $\text{NaOH}$  forming sodium meta-aluminate  $\text{Na}[\text{Al}(\text{OH})_4]$ .

10.  $\text{NaOH}$  can be used to separate  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$ .

11. Yellow ammonium sulphide (YAS) can be used to separate  $\text{SnS}$  and  $\text{As}_2\text{S}_3$ .

12.  $\text{NH}_4\text{SCN}$  can be used to make distinction between  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$ .

13.  $\text{NaOH}$  can be used to separate  $\text{Al}(\text{OH})_3$  and  $\text{Zn}(\text{OH})_2$ .

14. In II group, formation of whitish turbidity on dilution with  $\text{H}_2\text{O}$  indicates  $\text{Sb}^{3+}$ .

15. If acidified solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  turns green on addition of a salt then salt may contain  $\text{Fe}^{2+}$ .

16. White ppt. of  $\text{PbCl}_2$  is soluble in *aq.*  $\text{NH}_3$ .

17.  $\text{Hg}_2\text{Cl}_2$  is blackened by  $\text{NH}_3$  due to formation of iodide of Millon's base.

18.  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is used to test  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ions.

19. When  $\text{KNO}_2$  and  $\text{CH}_3\text{COOH}$  is added to  $\text{CoCl}_2$  solution, yellow ppt. of  $\text{K}_4[\text{Co}(\text{NO}_2)_6]$  is formed.

20. Alkaline solution of  $\text{NH}_4\text{Cl}$  gives brown ppt. with  $\text{K}_2\text{HgI}_4$ .

## Fill in the Blanks

- Separation of basic radicals is based on .....(a)..... and .....(b)..... .
- $\text{NH}_4\text{Cl}$  is added alongwith  $\text{NH}_4\text{OH}$  in group .....(a)..... to .....(b)..... concentration of .....(c)..... ion.
- Precipitation of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  takes place in presence of .....(a)..... by .....(b)..... .
- $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  are separated by .....(a)..... formation using .....(b)..... in which .....(c)..... is more stable

## True & False

- $\text{NH}_4\text{Cl}$  can be replaced by  $(\text{NH}_4)_2\text{SO}_4$  in group III.

than .....(d)..... ; on passing  $\text{H}_2\text{S}$  gas .....(e)..... is precipitated.

5.  $\text{PbCl}_2$  is soluble in .....(a)..... ,  $\text{AgCl}$  is soluble in .....(b)..... while  $\text{Hg}_2\text{Cl}_2$  is .....(c)..... by  $\text{NH}_3$ .

6. Copper subgroup ppt. and arsenic subgroup ppt are separated using.....(a)..... .

7. If orange turbidity appears on dilution with  $\text{H}_2\text{O}$  of the solution in dil.  $\text{HCl}$ , it is due to .....(a)..... and .....(b)..... ion is assumed confirmed.

8.  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$  ppt. can be separated by .....(a)..... when .....(b)..... becomes soluble due to the formation of .....(c)....., and .....(d)..... remains insoluble.

9.  $\text{Cr}(\text{OH})_3$  is made soluble in  $\text{NaOH}$  in presence of .....(a)..... when .....(b)..... of .....(c)..... colour is formed and gives yellow ppt. of .....(d)..... when .....(e)..... is added.

10. Reagent used to test  $\text{Ni}^{2+}$  ion is .....(a)..... .

11. Acidified  $\text{KMnO}_4$  can be decolourised by .....(a)..... .

12.  $\text{FeC}_2\text{O}_4$  can decolourise acidified  $\text{KMnO}_4$  due to the oxidation of .....(a)..... and .....(b)..... .

13. Ferric alum is the indicator in the titration of  $\text{Ag}^+$  with  $\text{SCN}^-$  when .....(a)..... colour appears at the end point.

14.  $\text{Fe}^{2+}$  gives blue colour, called .....(a)..... with .....(b)..... while  $\text{Fe}^{3+}$  gives blue colour, called .....(c)..... with .....(d)..... .

15. A reagent that can detect any of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  is .....(a)..... .

16.  $\text{PbSO}_4$  is soluble in .....(a)..... due to formation of .....(b)..... .

17.  $\text{Al}(\text{OH})_3$  is precipitated if its ionic product .....(a)..... is .....(b)..... than  $K_{sp}$ .

18.  $\text{HgCl}_2$  gives orange ppt with .....(a)..... , which dissolves in excess of it forming .....(b)..... called .....(c)..... .

19.  $\text{NH}_4\text{SCN}$  gives red colour with .....(a)..... due to the formation of .....(b)..... .

20. Gas that turns lime water milky and acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  green is .....(a)..... .

21. Iron (II) sulphide gives foul smell of .....(a)..... in presence of moisture.

22.  $\text{AgBr}$  is soluble in hypo forming .....(a)..... .

23.  $\text{NO}_3^-$  is detected by .....(a)..... when .....(b)..... is formed on the addition of  $\text{FeSO}_4$  and conc.  $\text{H}_2\text{SO}_4$ .

24.  $\text{Cl}^-$  is confirmed by .....(a)..... .

25. Addition of one drop of  $\text{HNO}_3$  in group (III) analysis is to .....(a)..... .

26. Reagent that can detect any of  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  is .....(a)..... .

27. While testing borate, green edged flame is due to formation of .....(a)..... .

28. When  $\text{SO}_2$  is passed into suspension of  $\text{CaSO}_3$  in water, .....(a)..... is formed.

29. Alkaline  $\text{NH}_4^+$  salt gives brown ppt. with  $\text{K}_2\text{HgI}_4$ ; brown ppt is called .....(a)..... .

30. Even in the absence of group II, colloidal yellowish ppt appears on passing  $\text{H}_2\text{S}$  gas; it may be due to the presence of .....(a)..... .

31. Yellow ppt of .....(a)..... is formed when  $\text{CoCl}_2$  reacts with excess of  $\text{KNO}_2$  in presence of  $\text{CH}_3\text{COOH}$ .

32.  $\text{BaBr}_2$  in aqueous solution gives yellow ppt with .....(a)..... as well as with .....(b)..... .

33. Sodium carbonate and mixture are taken in .....(a)..... ratio while preparing sodium carbonate extract.

34.  $\text{Hg}_2\text{Cl}_2$  is precipitated if .....(a)..... is greater than  $K_{sp}(\text{Hg}_2\text{Cl}_2)$ .

35.  $\text{AgCl}$  is soluble in .....(a)..... and  $\text{Ag}^+$  is present in .....(b)..... .

36.  $\text{Cu}^{2+}$  gives white ppt of .....(a)..... with .....(b)..... and deep blue colour of .....(c)..... with .....(d)..... .

37. On heating the salt with  $\text{HNO}_3$  and ammonium molybdate, formation of yellow ppt indicates the presence of .....(a)..... or .....(b)..... .

38.  $\text{As}_2\text{S}_3$  is soluble in  $(\text{NH}_4)_2\text{S}_2$  (yellow ammonium sulphide) due to the formation of .....(a)..... .

39. Reddish brown colouration when neutral  $\text{FeCl}_3$  is added to the  $\text{CH}_3\text{COO}^-$  aqueous solution is due to the formation of .....(a)..... .

40. Hypo gives .....(a)..... ppt with  $\text{AgNO}_3$  which changes to .....(b)..... .

## Matrix-Match Type Questions

### Only One Correct

1. Match the set of ion and reagent (in List I) with colour obtained (in list II).

| List I                                              | List II       |
|-----------------------------------------------------|---------------|
| A. $\text{Fe}^{3+} + [\text{Fe}(\text{CN})_6]^{4-}$ | 1. Cherry red |
| B. $\text{Fe}^{3+} + \text{CNS}^-$                  | 2. Pink       |
| C. $\text{Ni}^{2+} + \text{DMG}$                    | 3. Blood red  |
| D. $\text{CrO}_4^{2-} + \text{Pb}^{2+}$             | 4. Blue       |
| E. $\text{Mn}^{2+} + \text{PbO}_2 + \text{H}^+$     | 5. Yellow ppt |

**One or More Correct**

1. Match the reagents (in List I) with the cations (in List II) which can be identified.

| List I                  | List II      |
|-------------------------|--------------|
| A. $K_4[Fe(CN)_6]$      | 1. $Zn^{2+}$ |
| B. $NH_4CNS$            | 2. $Fe^{3+}$ |
| C. $CH_3COONa$          | 3. $Cu^{2+}$ |
| D. $H_2S/H^+$           | 4. $Cd^{2+}$ |
| E. $H_2S/NH_2OH-NH_4Cl$ | 5. $Ni^{2+}$ |

2. Match the reagents (in List I) with the cations (in List II) which can be identified.

| List I             | List II         |
|--------------------|-----------------|
| A. $AgNO_3$        | 1. $Cl^-$       |
| B. $FeCl_3$        | 2. $Br^-$       |
| C. $BaCl_2$        | 3. $I^-$        |
| D. $(CH_3COO)_2Pb$ | 4. $CH_3COO^-$  |
| E. $Cl_2$ water    | 5. $CrO_4^{2-}$ |

3. Match the set of basic radicals (in List I) with the group reagent (in List II) and analytical group (in List III).

| List I                | List II                  | List III |
|-----------------------|--------------------------|----------|
| A. $Zn^{2+}, Ni^{2+}$ | 1. $H_2S/H^+$            | P. I     |
| B. $Ag^+, Hg_2^{2+}$  | 2. $(NH_4)_2CO_3/NH_4OH$ | Q. II    |
| C. $Ca^{2+}, Ba^{2+}$ | 3. $H_2S/NH_4OH, NH_4Cl$ | R. III   |
| D. $Cu^{2+}, Cd^{2+}$ | 4. dil. $HCl$            | S. IV    |
| E. $Al^{3+}, Cr^{3+}$ | 5. $NH_4Cl/NH_4OH$       | T. V     |

4. Match the reagents (in List I) with cations (in List II) which can be identified.

| List I              | List II      |
|---------------------|--------------|
| A. $KMnO_4/H^+$     | 1. $Ca^{2+}$ |
| B. $K_2Cr_2O_7/H^+$ | 2. $Ag^+$    |
| C. $(NH_4)_2C_2O_4$ | 3. $Pb^{2+}$ |
| D. $KI$             | 4. $Fe^{3+}$ |
| E. $K_2CrO_4$       | 5. $Ba^{2+}$ |

**Integer Answer Types**

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the ORS have to be darkened. For example, if the correct answers to question number X, Y, Z and W (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will like the following

| X | Y | Z | W |
|---|---|---|---|
| ① | ① | ① | ① |
| ② | ② | ② | ② |
| ③ | ③ | ③ | ③ |
| ④ | ④ | ④ | ④ |
| ⑤ | ⑤ | ⑤ | ⑤ |
| ⑥ | ⑥ | ⑥ | ⑥ |
| ⑦ | ⑦ | ⑦ | ⑦ |
| ⑧ | ⑧ | ⑧ | ⑧ |
| ⑨ | ⑨ | ⑨ | ⑨ |

**Set I**

- $SO_2$  turns acidified  $K_2Cr_2O_7$  solution green. Oxidation number of the green-coloured ion is .....
- Brown coloured ring formed in the nitrate test has formula  $[Fe(H_2O)_5NO]SO_4$ . Unpaired electrons in Fe is .....
- In question (2) magnetic moment is  $\sqrt{x}$  where x is .....
- Aqueous neutral solution of  $FeCl_3$  reacts and acetate to form a reddish brown colour compound  $[Fe_3(OH)_2(CH_3COO)_x]^+$ , where x is .....
- $FeCl_3$  gives blood red colour of formula  $[Fe(CNS)(H_2O)_y]^+$  with  $KCNS$ . Here y = .....
- Copper metaborate is formed in the test of copper ion in borax-bead test. Number of boron atoms in copper metaborate is .....
- $AgBr$  dissolved in  $Na_2S_2O_3$ . 1 mol of  $AgBr$  is dissolved in x mol of  $Na_2S_2O_3$ . Where x is .....
- Blue coloured precipitate of Prussian blue has total of iron atom(s) .....

**Set II**

This section contains 10 questions

Each number in the following represents a colour give the answer in the form of number related to that colour formed in cation/anion analysis.

- |           |                  |
|-----------|------------------|
| 1. White  | 6. Black         |
| 2. Blue   | 7. Grey          |
| 3. Milky  | 8. Green         |
| 4. Orange | 9. Buff coloured |
| 5. Yellow | 0. Reddish brown |

- $H_2S$  gas is passed into aqueous  $CdCl_2$  solution
- $H_2S$  gas is passed into aqueous zinc acetate solution
- $SO_2$  gas is passed into lime water
- $SbCl_3$  solution is diluted with  $H_2O$
- $H_2S$  gas is passed into lead-acetate solution
- $NH_4OH$  is added to  $CrCl_3$  solution in presence of  $NH_4Cl$
- $H_2S$  gas is passed into  $MnCl_2$  solution in presence of  $NH_4Cl$  and  $NH_4OH$
- $KI$  is added to acidified  $K_2Cr_2O_7$  solution
- $SnCl_2$  is added to  $HgCl_2$  solution
- $K_4[Fe(CN)_6]$  is added to  $FeCl_3$  solution



21. (A):  $\text{NH}_4\text{NO}_2$  (B):  $\text{NH}_3$  (C):  $\text{NaNO}_3$  (D):  $\text{N}_2$   
(E):  $\text{AlN}$

22. (A) :  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (B) :  $\text{NH}_3$  (C) :  $\text{Cr}_2\text{O}_3$  (D) :  $\text{N}_2$   
 (E) :  $\text{AlN}$  (F) :  $\text{CrCl}_3$  (G) :  $\text{Na}_2\text{CrO}_4$  (H) :  $\text{PbCrO}_4$
23.  $\text{AsO}_4^{2-}; \text{Mg}^{2+} + \text{NH}_4^+ + \text{AsO}_4^{2-} \longrightarrow \text{MgNH}_4\text{AsO}_4$   
 white ppt
24. (a)  $\text{KI} + \text{HgI}_2 + \text{NaOH}$   
 or  $\text{KI}(\text{excess}) + \text{HgCl}_2 + \text{NaOH}$   
 (b)  $\text{NH}_4^+$  salts (c) Refer text for reaction

### Analytical Questions

| 1.                   | %     | Mole | Ratio |
|----------------------|-------|------|-------|
| $\text{Co}^{3+}$     | 21.24 | 0.36 | 1     |
| $\text{NH}_3$        | 24.77 | 1.46 | 4     |
| $\text{Cl}^-$        | 12.81 | 0.36 | 1     |
| $\text{SO}_4^{2-}$   | 34.65 | 0.36 | 1     |
| $\text{H}_2\text{O}$ | 6.53  | 0.36 | 1     |

Thus, empirical formula is  $[\text{Co}(\text{NH}_3)_4\text{ClSO}_4] \cdot \text{H}_2\text{O}$

2. (A) :  $\text{CuFeS}_2$ , (B) :  $\text{CuSO}_4$ , (C) :  $\text{FeSO}_4$ , (D) :  $\text{H}_2\text{S}$   
 (E) :  $\text{CuS}$ , (F) :  $\text{Cu}(\text{NO}_3)_2$ , (G) :  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$   
 (H) :  $\text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ , Turnbull's blue
3. (A) :  $\text{Pb}(\text{NO}_3)_2$ , (B) :  $\text{PbCl}_2$ , (C) :  $\text{PbS}$ , (D) :  $\text{PbI}_2$
4. (A) :  $\text{ZnCO}_3$ , (B) :  $\text{CO}_2$ , (C) :  $\text{ZnO}$ , (D) :  $\text{ZnS}$ ,  
 (E) :  $\text{Zn}(\text{OH})_2$
5. (A) :  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , (B) :  $\text{SO}_2$ , (C) :  $\text{SO}_3$ ,  
 (D) :  $\text{Fe}_2\text{O}_3$ , (E) :  $\text{BaSO}_4$
6. (X) is  $2\text{MHCO}_3 \longrightarrow \text{M}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$   
 $2(m+61) \text{ g} \qquad \qquad \qquad 44 \text{ g}$   
 $\frac{2(m+61)}{20.02} = \frac{44}{4.4}$   
 Thus,  $M = 39.1$   
 (X) :  $\text{KHCO}_3$ , (Y) :  $\text{K}_2\text{CO}_3$ , (Z) :  $\text{BaCO}_3$ , (A) :  $\text{CO}_2$ ,  
 (B) :  $\text{H}_2\text{O}$
7. (A) :  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , (B) :  $\text{FeSO}_4$ ,  
 (C) :  $\text{FeSO}_4 \cdot \text{NO}$  or  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$   
 (D) :  $\text{Fe}_2\text{O}_3$ , (E) :  $\text{SO}_2$ , (F) :  $\text{SO}_3$
8. (A) :  $\text{NH}_4\text{NO}_2$ , (B) :  $\text{NH}_3$ , (C) :  $\text{NaNO}_3$ ,  
 (D) :  $\text{NaNH}_2$ , (E) :  $\text{N}_2\text{O}$ , (F) :  $\text{N}_3\text{Na}$  (sodium azide)  
 (G) :  $\text{N}_3\text{H}$  (hydroazoic acid)
9. Molar mass of acid of phosphorus  $\times$  molarity = g/L

$$\text{Molar mass} \times 0.1 = 9.8 \text{ g L}^{-1}$$

$$\therefore \text{Molar mass of acid} = 98 \text{ g mol}^{-1}$$

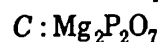
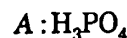
Let basicity of acid be =  $x$ ,

$$\text{then } 0.1 \text{ M acid} = 0.1 \times x \text{ N}$$

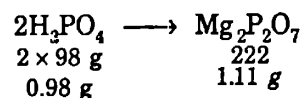
$$100 \times 0.1 \times x = 300 \times 0.1 \text{ N NaOH}$$

$$x = 3$$

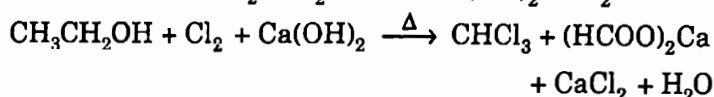
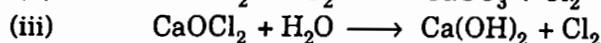
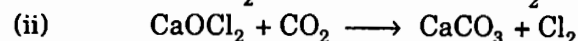
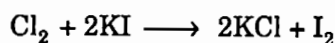
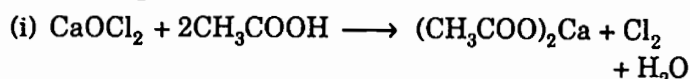
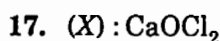
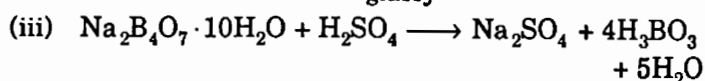
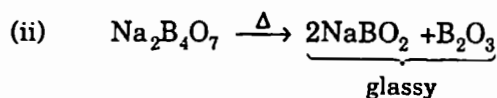
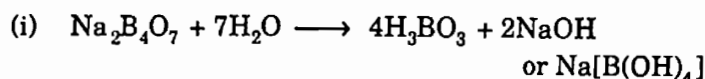
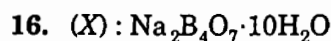
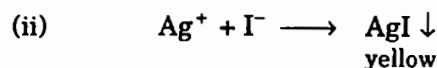
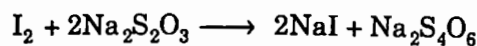
Thus, acid is tribasic which is  $\text{H}_3\text{PO}_4$ .



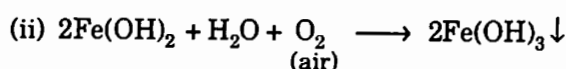
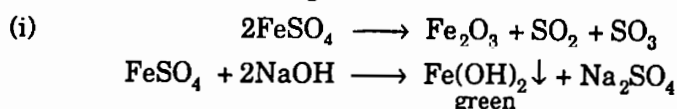
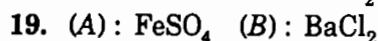
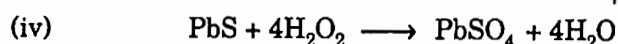
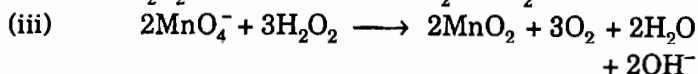
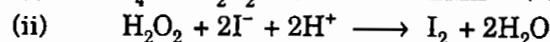
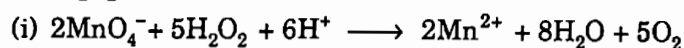
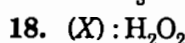
Identify if C is confirmed by the following reaction



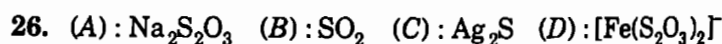
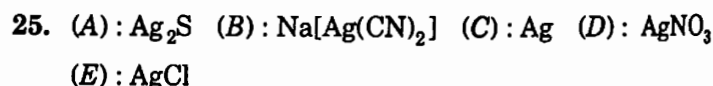
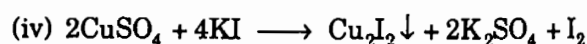
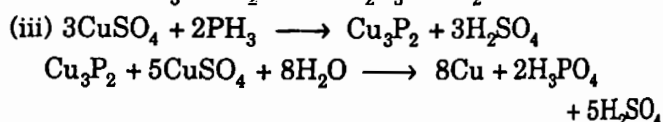
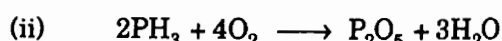
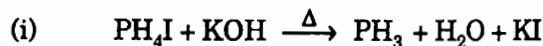
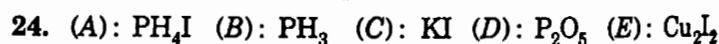
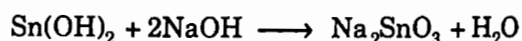
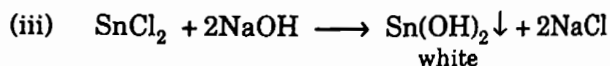
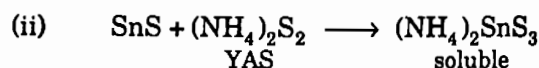
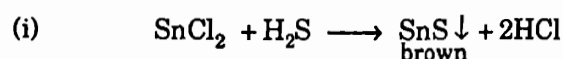
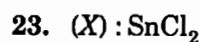
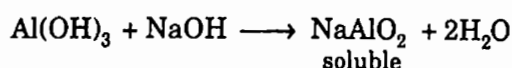
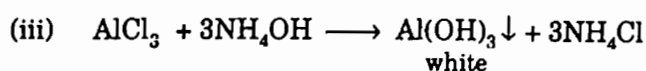
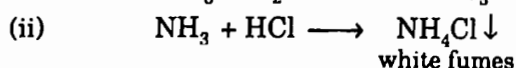
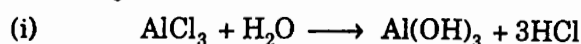
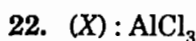
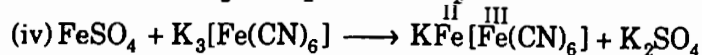
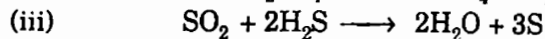
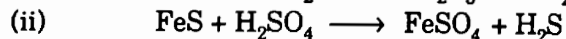
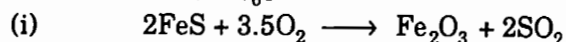
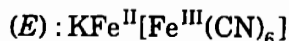
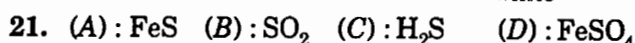
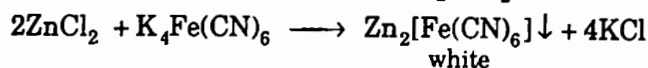
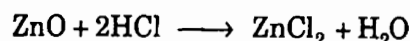
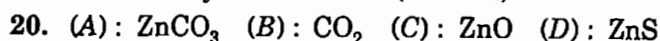
10. (A) :  $\text{H}_2\text{S}_2\text{O}_8$  (Marshall's acid), (B) :  $\text{H}_2\text{SO}_4$ ,  
 (C) :  $\text{H}_2\text{O}_2$ , (D) :  $\text{BaSO}_4$
11. (A) :  $\text{Ag}$ , (B) :  $\text{AgNO}_3$ , (C) :  $\text{NO}_2$ , (D) :  $\text{AgCl}$ ,  
 (E) :  $\text{Ag}_2\text{S}_2\text{O}_3$ , (F) :  $\text{Ag}_2\text{S}$
12. (X) :  $\text{SO}_2$   
 (i)  $3\text{SO}_2 + \text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + \text{H}_2\text{O} + 3\text{SO}_4^{2-}$   
 (ii)  $\text{SO}_2 + \text{H}_2\text{O}_2 \longrightarrow \text{SO}_4^{2-} + 2\text{H}^+$   
 $\text{SO}_4^{2-} + \text{Ba}^{2+} \longrightarrow \text{BaSO}_4 \downarrow$   
 (iii)  $2\text{H}_2\text{S} + \text{SO}_2 \longrightarrow 3\text{S} + 2\text{H}_2\text{O}$
13. (a) (X) :  $\text{NaOH}$   
 (i)  $\text{Zn} + 2\text{NaOH} \longrightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2$   
 (ii)  $\text{SnCl}_2 + 2\text{NaOH} \longrightarrow \text{Sn}(\text{OH})_2 \downarrow$   
 white  
 $\text{Sn}(\text{OH})_2 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{SnO}_2 + 2\text{H}_2\text{O}$   
 soluble
- (b)  $\text{Na}_2\text{B}_4\text{O}_7 \xrightarrow{\Delta} 2\text{NaBO}_2 + \text{B}_2\text{O}_3$   
 $2\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3 + 14\text{H}_2\text{O}$   
 $\text{Fe}_2\text{O}_3 + 3\text{B}_2\text{O}_3 \longrightarrow 2\text{Fe}(\text{BO}_2)_3$   
 yellow
14. (X) :  $\text{HgCl}_2$   
 (i)  $\text{HgCl}_2 + \text{H}_2\text{S} \longrightarrow \text{HgS} + 2\text{HCl}$   
 (iii)  $2\text{HgCl}_2 + \text{SnCl}_2 \longrightarrow \text{Hg}_2\text{Cl}_2 \downarrow + \text{SnCl}_4$   
 white  
 $\text{Hg}_2\text{Cl}_2 + \text{SnCl}_2 \longrightarrow 2\text{Hg} \downarrow + \text{SnCl}_4$   
 grey
- (iv)  $\text{HgCl}_2 + 2\text{KI} \longrightarrow \text{HgI}_2 \downarrow$   
 orange  
 $\text{HgI}_2 + 2\text{KI} \longrightarrow \text{K}_2\text{HgI}_4$   
 soluble
15. (a) (X) :  $\text{NH}_3$   
 (i)  $\text{NH}_3$  turns red litmus blue  
 (ii)  $\text{CuSO}_4 + 4\text{NH}_3 \longrightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4$   
 deep blue  
 (iii)  $\text{FeCl}_3 + 3\text{NH}_4\text{OH}(\text{aq}) \longrightarrow \text{Fe}(\text{OH})_3 + 3\text{NH}_4\text{Cl}$   
 soluble  
 $\text{Fe}(\text{OH})_3 + 3\text{HNO}_3 \longrightarrow \text{Fe}(\text{NO}_3)_3 + 3\text{H}_2\text{O}$   
 soluble
- (b) (X) :  $\text{KI}$   
 (i)  $2\text{CuSO}_4 + 4\text{KI} \longrightarrow \text{Cu}_2\text{I}_2 \downarrow + \text{I}_2 + 2\text{K}_2\text{SO}_4$   
 white



$\text{CHCl}_3$  is an anaesthetic.

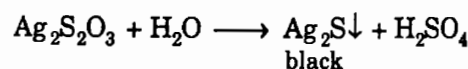
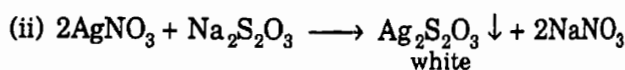
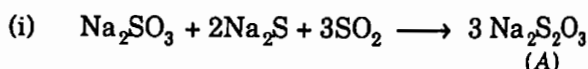


(v) Chromyl chloride test (see text)

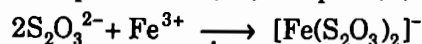


(violet, immediately changes to colourless)

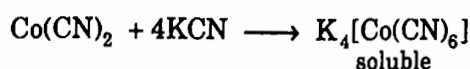
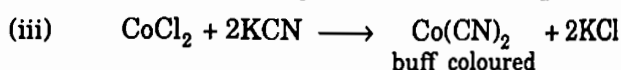
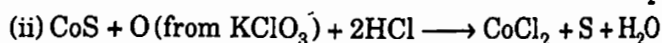
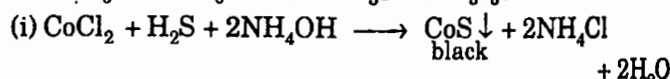
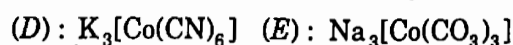
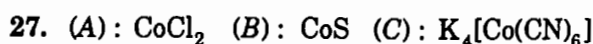
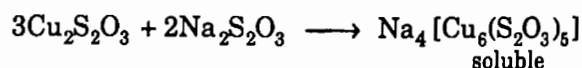
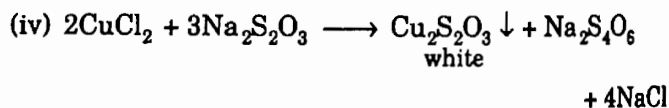
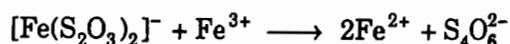
(E) :  $\text{Na}_4[\text{Cu}_6(\text{S}_2\text{O}_3)_5]$  sodium cupro (I) thiosulphate complex.

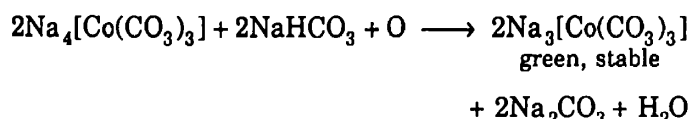
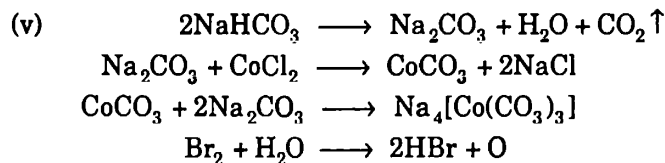
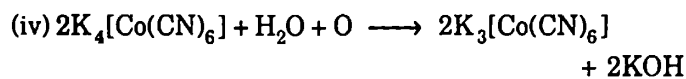


(iii) A dark violet coloration is due to formation of dithiosulphato iron (III) complex (D)

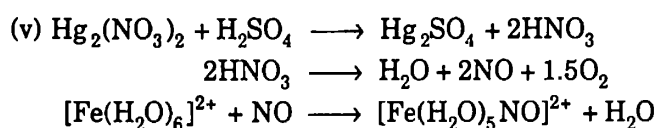
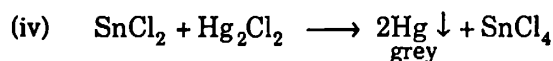
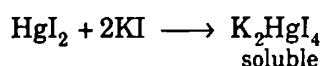
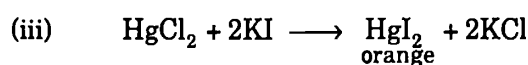
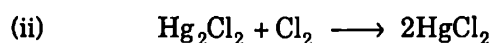
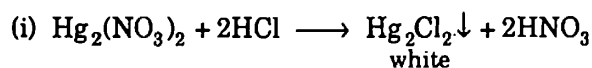


This colour disappears rapidly due to formation of  $\text{S}_4\text{O}_6^{2-}$  and  $\text{Fe}^{2+}$



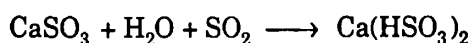
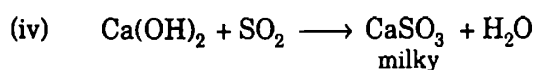
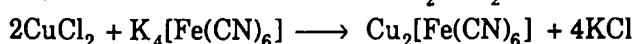
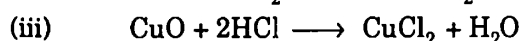
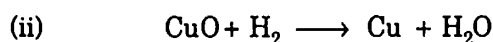
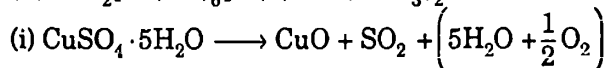


28. (A) :  $Hg_2(NO_3)_2$  (B) :  $Hg_2Cl_2$  (C) :  $HgCl_2$  (D) :  $K_2HgI_4$   
(E) :  $Hg$  (F) :  $FeSO_4 \cdot NO$



29. (A) :  $CuSO_4 \cdot 5H_2O$  (B) :  $CuO$  (C) :  $SO_2$  (D) :  $Cu$

(E) :  $Cu_2[Fe(CN)_6]$  (F) :  $Ca(HSO_3)_2$



30. (A) :  $CdS$  (B) :  $CdSO_4$  (C) :  $[Cd(NH_3)_4]^{2+}$

(D) :  $K_2[Cd(CN)_4]$  (E) :  $BaSO_4$

31. (A) :  $FeCl_3$  (B) :  $[Fe(SCN)]Cl_2$  (C) :  $KFe^{III}[Fe^{II}(CN)_6]$   
Prussian blue

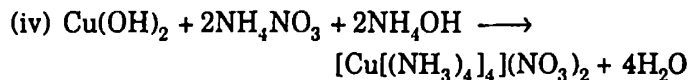
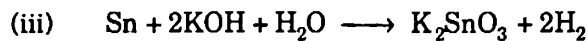
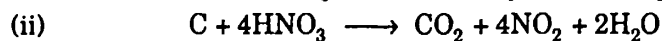
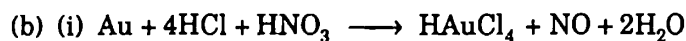
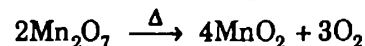
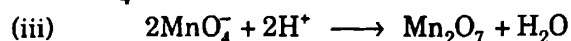
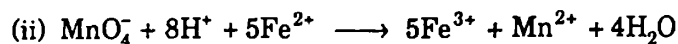
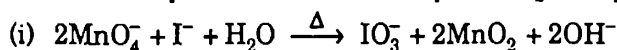
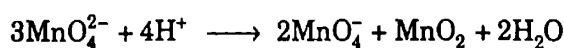
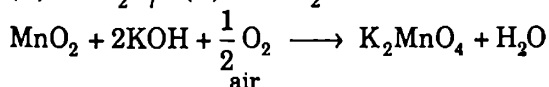
(D) :  $CrO_2Cl_2$  (E) :  $BaCrO_4$

(similar reactions given earlier.)

Note : Actual red colour of (B) is a mixture of  $[Fe(SCN)(H_2O)_5]^{2+}$  and also some  $Fe(SCN)_3$  and  $[Fe(SCN)_4]^-$ .

32. (a) (A) :  $K_2MnO_4$  (B) :  $KMnO_4$  (C) :  $KIO_3$

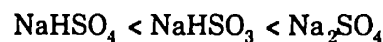
(D) :  $Mn_2O_7$  (E) :  $MnO_2$



33. Label them yourself as (A) for  $AlCl_3 \cdot 6H_2O$  (B) for  $Ba(OH)_2 \cdot 8H_2O$  and (C) for  $MgSO_4 \cdot H_2O$ .

[(A), (B), and (C) are unknown till confirmed]; mix (B) and (C) white ppt confirms that one of them is  $Ba(OH)_2$  and the other  $MgSO_4$ . Add (B) and (C) each to (A) (which is certainly  $AlCl_3 \cdot 6H_2O$ ) of white ppt [of  $Al(OH)_3$ ] then that compound is (B).

34. By measurement of pH, which would be in order



35. (a) sulphur (b)  $P_2O_5$  (c) CO (d) Si

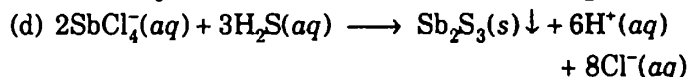
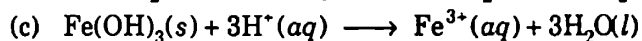
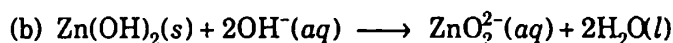
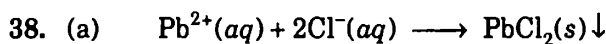
36. (a)

37. If  $Hg_2Cl_2$ ,  $AgCl$  and  $PbCl_2$  are precipitated then,

(a)  $PbCl_2$  remains insoluble

(b)  $Hg_2Cl_2$  is blackened by addition of  $NH_3$  due to formation of  $(Hg + HgNH_2Cl)$

(c)  $AgCl$  goes into solution as soluble complex  $[Ag(NH_3)_2]Cl$



39. A :  $Cd(CH_3COO)_2$ , B :  $[Fe(CH_3COO)]^{2+}$ , C :  $CdS$ ,  
D :  $[Cd(NH_3)_4]^{3+}$ , E :  $[Cd(CN)_4]^{2-}$

40. A :  $NaBO_2$ , B :  $CO_2$ , C :  $Na_2B_4O_7$ , D :  $B_2O_3$ ,  
E :  $H_3BO_3$ , F :  $Co(BO_2)_2$ , G :  $(C_2H_5O)_3B$

41. A :  $ZnS$ , B :  $H_2S$ , C :  $ZnSO_4$ , D :  $PbS$ ,  
E :  $Zn(OH)_2$ , F :  $Na_2ZnO_2$  or  $Na_2[Zn(OH)_4]$

42.  $X_2$  is decolourised by unsaturated hydrocarbon thus,  $X_2$  is  $Br_2$  and  $MX$  is  $MBr$ .

Depression in freezing point

$$(\Delta T_f) = 0 - (-3.72^\circ) = 3.72^\circ$$

$$\Delta T_f = \frac{1000 K_f w_1(i)}{m_1 w_1}$$

$m_1$  (molar mass of  $MBr$ ) = ?

$K_f$  (molar depression constant) =  $1.86^\circ \text{ mol}^{-1} \text{ kg}$

$w_1$  (mass of  $MX$ ) = 11.9 g

$w_2$  (mass of  $H_2O$ ) = 100 g

$$i \text{ (van't Hoff factor)} = (1 + x) = 1 + 1 = 2$$

$$x = \text{degree of ionisation} = 1$$

(assuming  $MX$  is conducting and 100% ionised.)

$$\therefore m_1 = \frac{1000 \times 1.86 \times 11.9 \times 2}{3.72 \times 100}$$

$$= 119 \text{ g mol}^{-1}$$

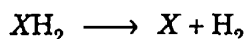
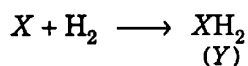
$$\therefore \text{Thus, } M + \text{Br} = 119 \text{ g mol}^{-1}$$

$$\therefore M + 80 = 119$$

$$M = 39$$

Thus,  $M$  is potassium.

43. Element  $X$  belong to group 2, thus it forms divalent cation  $X^{2+}$



559 g mL of  $H_2$  combines with = 1 g  $X$

$\therefore$  22400 mL of  $H_2$  combines with = 40 g  $X$

Thus, atomic mass of  $X = 40 \text{ g mol}^{-1}$

Thus,  $X$  is Ca,  $Y$  is  $CaH_2$  and  $Z$  is  $CaCl_2$

It is confirmed by the fact that

$$\% \text{ of chlorine in } CaCl_2 = \frac{71 \times 100}{111}$$

$$= 63.96 \approx 63.89 \text{ (given)}$$

44.  $X$ : Sn or Pb,  $Y$ : P,  $Z$ : alkali metal

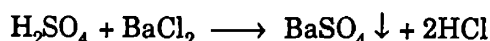
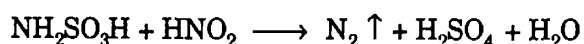
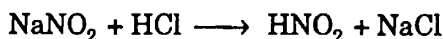
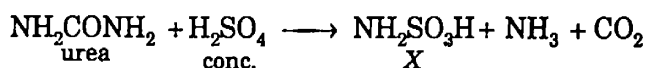
45. (a)  $NH_2OH$  is reduced to  $NH_3$

(b)  $HPO_3^{2-}$  is oxidised to  $HPO_4^{2-}$

(c) Initially  $H_3PO_2$  is oxidised to  $H_3PO_3$  and finally to  $H_3PO_4$

In the reactions above, total change in oxidation number in oxidation reaction is equal to that in reduction reaction.

46.  $X$ :  $NH_2SO_3H$



47.  $A$ :  $Na_2S_2O_3$ ;  $B$ :  $Ag_2S_2O_3$ ;  $C$ :  $Na_3[Ag(S_2O_3)_2]$

$D$ :  $Ag_2S$ ;  $E$ :  $H_2SO_4$ ;  $F$ :  $BaSO_4$

48.  $BaMnO_4 \equiv Ba^{2+} + MnO_4^{2-}$

Thus,  $MnO_4^-$  is reduced to  $MnO_4^{2-}$   
(+7) (+6)

Change in oxidation number =  $7 - 6 = 1$  unit

$$\text{Moles of } MnO_4^- \text{ used} = \frac{10 \times 0.1}{1000} = 0.001$$

$\therefore$  Equivalent of  $MnO_4^-$  used = 0.001

Let  $I^-$  be oxidised to species with oxidation number =  $x$



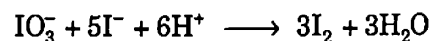
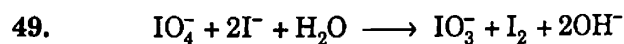
Change in oxidation number =  $x - (-1)$

$$\text{Equivalent of } I^- = \frac{0.01587}{127} = (x + 1)$$

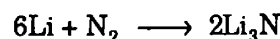
$$\therefore \frac{0.01587(x + 1)}{127} = 0.001$$

$$\therefore x = 7$$

Thus, iodide is oxidised to  $IO_4^-$ .



50.  $N_2$  can't be used with lithium since it reacts giving nitride.

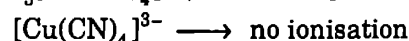
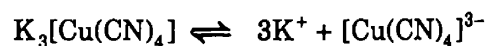
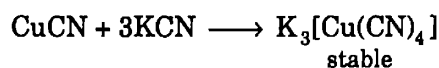
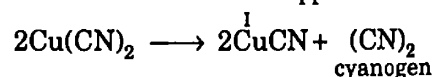
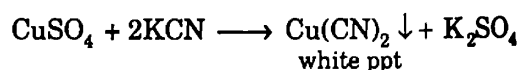
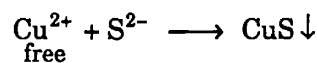


51.  $A$ :  $MgO$ ;  $B$ :  $MgCl_2$ ;  $C$ :  $MgCO_3$ ;  $D$ :  $CO_2$ ;

$E$ :  $MgO$ ;  $F$ :  $CaCO_3$ ;  $G$ :  $MgSO_4$ ;  $H$ :  $Mg(OH)_2$ ;

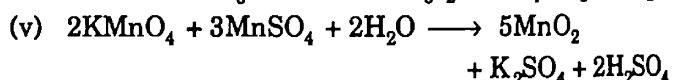
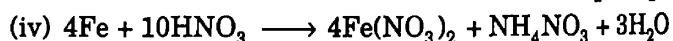
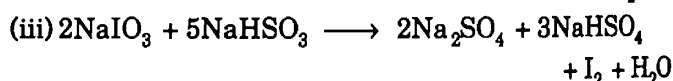
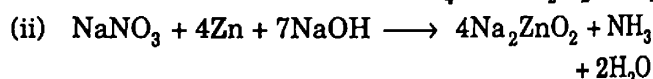
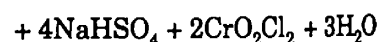
$I$ :  $Mg(NO_3)_2$ ;  $J$ :  $NO_2$

52. It is due to formation of a stable complex which does not ionise to give free  $Cu^{2+}$  that can give precipitate with  $H_2S$ .



53.  $M$  is potassium;  $KO_2$  is the most common superoxide.

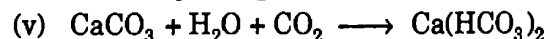
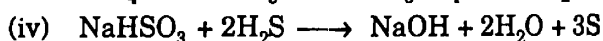
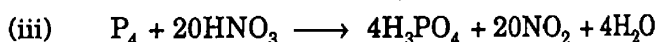
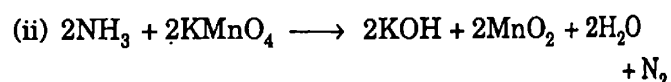
54. (i)  $K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4$



55. Radicals:  $Fe^{2+}$ ,  $NH_4^+$ ,  $SO_4^{2-}$ ,  $Cl^-$  (A):  $CrO_2Cl_2$

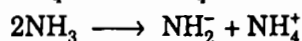
(B):  $KFe^{II}[Fe^{III}(CN)_6]$ , Turnbull's blue

56. (i)  $Na_2CO_3 + NO + NO_2 \longrightarrow 2NaNO_2 + CO_2$



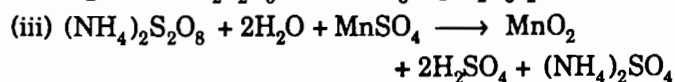
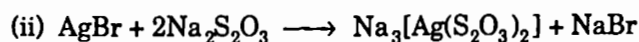
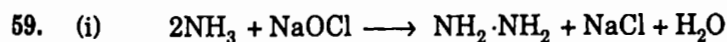
57. (i)  $\text{Al}(\text{OH})_3$  is soluble in  $\text{NaOH}$  forming  $\text{NaAlO}_2$ .

$\text{Fe}(\text{OH})_3$  is insoluble in  $\text{NaOH}$



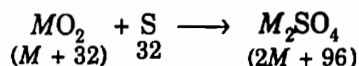
In  $\text{NH}_3$ ,  $\text{NH}_4^+$  is formed which is one of the ion of  $\text{NH}_4\text{Cl}$ .  $\text{NH}_4^+$  is an acid.

58.  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  (Mohr's salt)



60. (a) NO (b) NO (c)  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$

61. A is a binary salt of univalent metal A converts S to sulphate that A contains oxygen. Since, A is a binary salt thus A can be  $\text{MO}_2$  (superoxide) with  $\text{O}_2^-$  anion.



$$\frac{2M + 96}{32} = \frac{1.743}{0.321}$$

$$\therefore M = 38.87 \approx 39$$

Thus, binary compound

A is  $\text{KO}_2$ , B is  $\text{K}_2\text{SO}_4$ , C is  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  (alum)

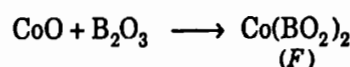
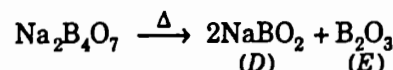
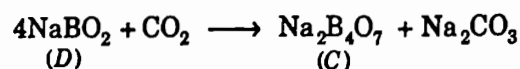
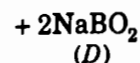
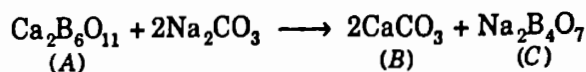
62. (A):  $\text{KO}_2$  (B):  $\text{K}_2\text{SO}_4$  (C):  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

63. (A):  $\text{O}_3$  (B):  $\text{KO}_3$  (C):  $\text{O}_2$

64. (A):  $\text{Pb}_3\text{O}_4$  (B):  $\text{PbO}_2$  (C):  $\text{PbI}_2$  (D):  $\text{HMnO}_4$  (pink)

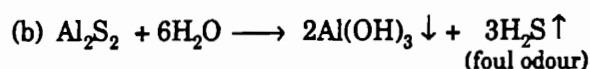
65. (A):  $\text{Ca}_2\text{B}_6\text{O}_{11}$  (B):  $\text{CaCO}_3$  (C):  $\text{Na}_2\text{B}_4\text{O}_7$

(D):  $\text{NaBO}_2$  (E):  $\text{B}_2\text{O}_3$  (F):  $\text{Co}(\text{BO}_2)_2$



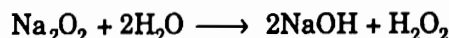
66. (A):  $\text{NH}_4\text{NO}_3$  (B):  $\text{N}_2\text{O}$  (C):  $\text{H}_2\text{O}$  (D):  $\text{P}_4\text{O}_{10}$

67. (a) (A): Ca (B):  $\text{Ca}_3\text{N}_2$  (C):  $\text{Ca}(\text{OH})_2$  (D):  $\text{NH}_3$



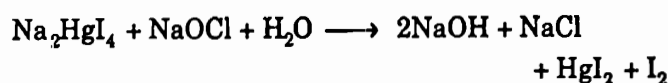
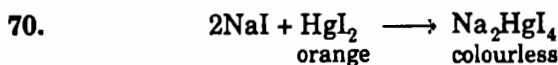
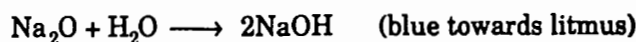
68. Refer Table 20.3

69. White solid is  $\text{Na}_2\text{O}_2$



Bleaching of litmus paper is due to  $\text{H}_2\text{O}_2$ .

If it would have been  $\text{Na}_2\text{O}$ , then its aqueous solution turned red litmus blue due to  $\text{NaOH}$ .



71. (a) (D):  $\text{H}_2\text{SO}_4$

(b) (A):  $\text{Ca}(\text{OH})_2$  (B):  $\text{NH}_4\text{HCO}_3$  (C):  $\text{Na}_2\text{CO}_3$

(D):  $\text{NH}_4\text{Cl}$  (E):  $\text{CaCl}_2$

## Exercise 2

### Only One Option Correct

- |          |          |          |          |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 1. (d)   | 2. (a)   | 3. (c)   | 4. (c)   | 5. (c)   | 6. (a)   | 7. (d)   | 8. (d)   | 9. (c)   | 10. (d)  |
| 11. (c)  | 12. (a)  | 13. (c)  | 14. (c)  | 15. (d)  | 16. (c)  | 17. (d)  | 18. (c)  | 19. (c)  | 20. (a)  |
| 21. (a)  | 22. (d)  | 23. (d)  | 24. (d)  | 25. (a)  | 26. (c)  | 27. (b)  | 28. (c)  | 29. (a)  | 30. (d)  |
| 31. (a)  | 32. (b)  | 33. (c)  | 34. (a)  | 35. (c)  | 36. (a)  | 37. (d)  | 38. (c)  | 39. (c)  | 40. (b)  |
| 41. (c)  | 42. (c)  | 43. (b)  | 44. (a)  | 45. (c)  | 46. (d)  | 47. (c)  | 48. (c)  | 49. (d)  | 50. (d)  |
| 51. (a)  | 52. (c)  | 53. (b)  | 54. (b)  | 55. (d)  | 56. (a)  | 57. (c)  | 58. (b)  | 59. (c)  | 60. (d)  |
| 61. (a)  | 62. (d)  | 63. (b)  | 64. (b)  | 65. (a)  | 66. (a)  | 67. (a)  | 68. (b)  | 69. (d)  | 70. (c)  |
| 71. (c)  | 72. (a)  | 73. (a)  | 74. (b)  | 75. (d)  | 76. (c)  | 77. (d)  | 78. (a)  | 79. (a)  | 80. (b)  |
| 81. (b)  | 82. (a)  | 83. (b)  | 84. (b)  | 85. (a)  | 86. (a)  | 87. (b)  | 88. (b)  | 89. (c)  | 90. (a)  |
| 91. (b)  | 92. (a)  | 93. (c)  | 94. (a)  | 95. (c)  | 96. (c)  | 97. (a)  | 98. (c)  | 99. (b)  | 100. (d) |
| 101. (b) | 102. (a) | 103. (c) | 104. (a) | 105. (c) | 106. (c) | 107. (d) | 108. (b) | 109. (a) | 110. (c) |
| 111. (c) | 112. (a) | 113. (d) | 114. (c) | 115. (b) | 116. (d) | 117. (b) | 118. (a) | 119. (c) | 120. (c) |
| 121. (a) | 122. (c) | 123. (b) | 124. (b) | 125. (a) | 126. (d) | 127. (a) | 128. (c) | 129. (c) | 130. (b) |
| 131. (a) | 132. (d) | 133. (b) | 134. (a) | 135. (d) | 136. (c) | 137. (b) | 138. (c) | 139. (b) | 140. (c) |

## One or More Than One Options Correct

1. (a,c,d)    2. (b,c)    3. (b,d)    4. (a,b)    5. (a,b)  
 6. (a,c)    7. (b,c,d)    8. (a,b,c,d)    9. (a,b,c)  
 10. (a,c,d)

## Brain Twisters

1. Reactions (i) to (iv) indicate that (A) is hypo  
 $\text{Na}_2\text{S}_2\text{O}_3 \cdot x\text{H}_2\text{O}$   
 hydrated

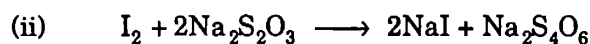
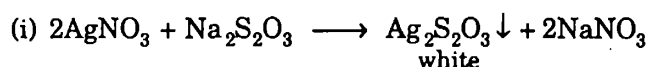
Mol. wt. of hypo (A) ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ) =  $158 + 18x$   
 and that of anhydrous hypo (B) ( $\text{Na}_2\text{S}_2\text{O}_3$ ) = 158

$$\frac{(A)}{(B)} = \frac{158 + 18x}{158} = \frac{2.48}{1.58}$$

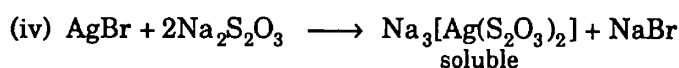
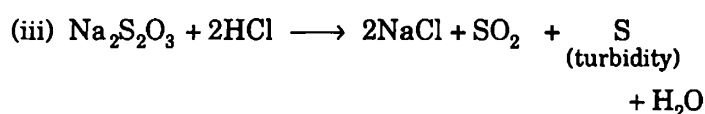
$$\Rightarrow x = 5$$

$$\Rightarrow (A) \text{ is } \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$$

**Explanation :**

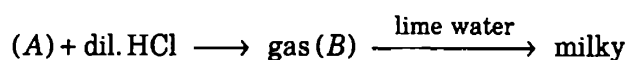


( $\text{I}_2$  is soluble in KI forming  $\text{KI}_3$ ;  $\text{I}_2$  is insoluble in  $\text{H}_2\text{O}$ )



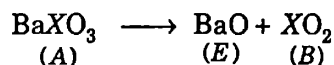
2. Paste of (A) is conc. HCl gave green colouration in flame.

$$\Rightarrow (A) \text{ has } \text{Ba}^{2+}$$



$\Rightarrow$  gas (B) can be either of  $\text{SO}_2$  or  $\text{CO}_2$

$\Rightarrow (A)$  can be  $\text{BaSO}_3$  or  $\text{BaCO}_3$  ( $\text{BaXO}_3$ ,  $X = \text{S}$  or  $\text{C}$ )



**Conformation of X :** ( $\text{Ba} = 137$ ,  $X = \text{X}$ ,  $\text{O} = 16$ )

$$\frac{\text{Ba} + X + 3(\text{O})}{\text{Ba} + \text{O}} = \frac{137 + X + 48}{137 + 16}$$

$$= \frac{1.9735}{1.5334}$$

$$\Rightarrow X = 11.91 \approx 12$$

Thus, (X) is carbon.

**Confirmation of Ba :** 1.5334 g of BaO [suppose it is unknown MO of molecular weight ( $M + 16$ )] where dissolved in 250 mL solution.

$$25 \text{ mL of MO} \equiv 20.30 \text{ mL of } 0.0985 \text{ M HCl}$$

$$\equiv 20.30 \text{ mL of } 0.0985 \text{ N HCl}$$

$$\text{N(MO)} = 0.08 \text{ N}$$

**MO :**

$$\text{Milliequivalent} = 0.08 \times 250$$

$$\text{equivalent} = \frac{0.08 \times 250}{1000} = 0.02$$

$$\text{mol} = 0.01$$

(since MO has divalent cation.)

$$\therefore \frac{\text{Amount}}{\text{molecular weight of MO}} = 0.01 \text{ mol}$$

$$\frac{1.5334 \text{ g}}{m} = 0.01$$

$$\therefore m = 153.34 \text{ g mol}^{-1} \text{ for MO}$$

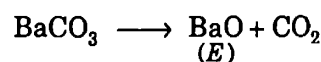
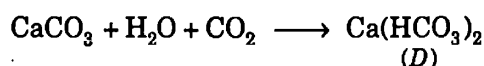
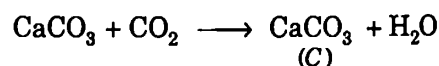
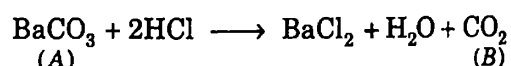
Thus, atomic weight of  $M = 153.34 - 16 = 137.34$

$\Rightarrow M$  is Ba

$\Rightarrow \text{MO}$  is BaO

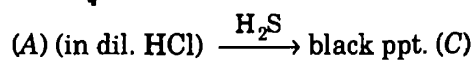
$\Rightarrow A$  is  $\text{BaCO}_3$

$\Rightarrow$  Molecular mass of  $\text{BaCO}_3 = 197.4 \text{ g mol}^{-1}$



3. (A) gives white ppt (B) with  $\text{BaCl}_2$  insoluble in conc. HCl

$\Rightarrow (A)$  has  $\text{SO}_4^{2-}$  ion



[insoluble in YAS (copper group)]

soluble in  $\text{HNO}_3$



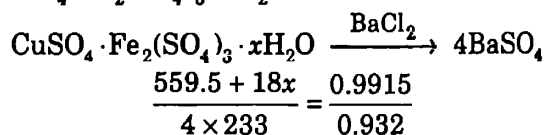
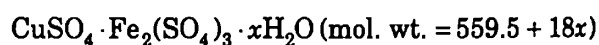
blue coloured solution (D)

$\Rightarrow (A)$  contains  $\text{Cu}^{2+}$

(A) gives brown ppt with  $(\text{NH}_4\text{Cl} + \text{NH}_4\text{OH})$  buffer indicating presence of  $\text{Fe}^{3+}$

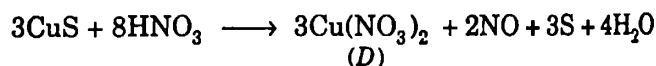
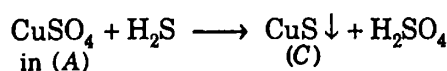
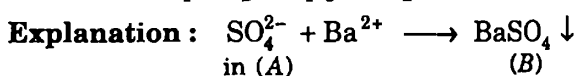
Thus, (A) contains  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{O}$

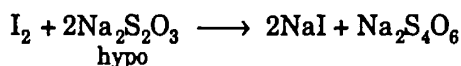
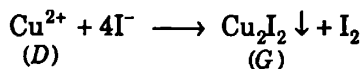
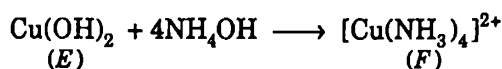
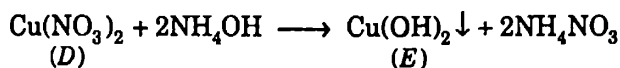
Since it is a double salt, it is a pseudo alum with probable formula



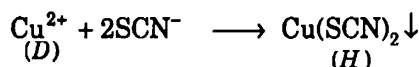
$$\Rightarrow x = 24$$

$\Rightarrow A$  is  $\text{CuSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

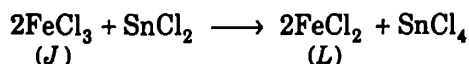
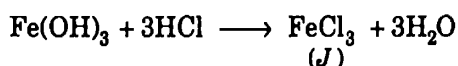
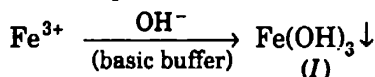




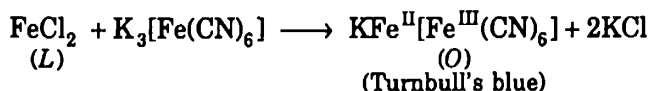
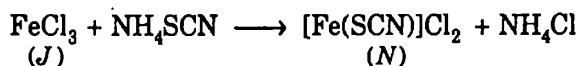
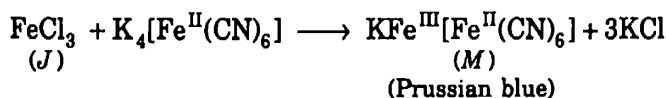
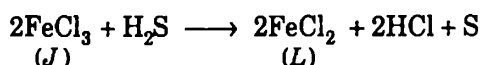
$\text{I}_2$  (before addition of hypo) remains dissolved in KI as  $\text{KI}_3$  (reddish brown). After hypo is added,  $\text{I}_2$  disappears and white ppt (G) appears.



Precipitate after separation of (C) contains  $\text{Fe}^{3+}$  ion

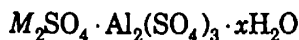


(L) is obtained from (J) by gas (K) (reducing agent) that can be  $\text{H}_2\text{S}$ .



4. (C) is hydrated double salt formed from (B) and  $\text{Al}_2(\text{SO}_4)_3$

$\Rightarrow$  (C) can be an Alum



(B) is obtained when S reacts with (A) in a sealed tube

$\Rightarrow$  (A) is also a source of oxygen that can convert S into  $\text{SO}_4^{2-}$ .

(A) has univalent cation  $M^+$  and its compound with oxygen can be

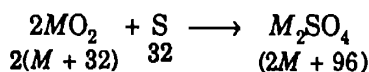
$M_2\text{O}$  (oxide)

$M_2\text{O}_2$  (peroxide)

$\text{MO}_2$  (superoxide)

Only  $\text{MO}_2$  is paramagnetic.

$\Rightarrow$  A is  $\text{MO}_2$  (binary given)



$2(M + 32)$  g  $\text{MO}_2$  reacts with 32 of sulphur

$$\therefore 1.422 \text{ g } \text{MO}_2 \text{ reacts with } \frac{32}{2(M + 32)} \times 1.422 \text{ g sulphur}$$

$$= \frac{32 \times 1.422}{2(M + 32)} = 0.321 \text{ g sulphur}$$

$$\Rightarrow M = 39 \text{ (K)}$$

$\Rightarrow$  (A) is  $\text{KO}_2$

(B) is  $\text{K}_2\text{SO}_4$

(C) is  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  (potash alum)

[Value of  $M$  can also be evaluated by using weight of  $\text{M}_2\text{SO}_4$  (i.e., 1.743 g (given))]

$$\frac{\text{weight of S}}{\text{weight of } \text{M}_2\text{SO}_4} = \frac{32}{(2M + 96)}$$

$$\frac{0.321}{1.743} = \frac{32}{2M + 96}$$

5. (A) +  $\text{BaCl}_2$  solution  $\longrightarrow$  white ppt (B)

$\Rightarrow \text{SO}_4^{2-}$  is present

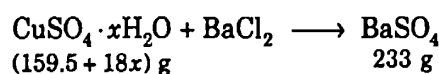
(A) + dil.  $\text{HCl} + \text{H}_2\text{S} \longrightarrow$  black ppt soluble in 50%  $\text{HNO}_3$

$\Rightarrow$  group II (copper subgroup) except  $\text{Hg}^{2+}$

(A) + aq  $\text{NH}_3$  (excess)  $\longrightarrow$  deep blue solution (C)

$\Rightarrow \text{Cu}^{2+}$  is present.

Thus, (A) is  $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$

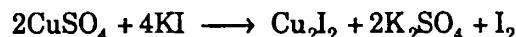
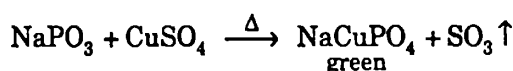
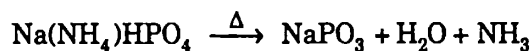
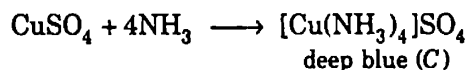


$$\frac{159.5 + 18x}{233} = \frac{2.495}{2.33}$$

$$\Rightarrow x = 5$$

Thus, (A) is  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

**Explanation :**



6. Let metal by (A).

(A) forms metal nitrate which gives red colouration to a non-luminous Bunsen burner.

$\Rightarrow$  (A) is Li (atomic weight 7)

metal nitrate is  $\text{LiNO}_3$

metal oxide (B) is  $\text{Li}_2\text{O}$

(C) is  $\text{Li}_3\text{N}$

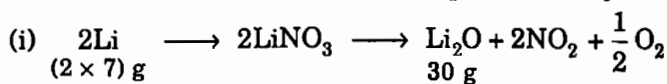
(D) is  $\text{LiH}$

(E) is  $\text{H}_2$

(F) is  $\text{LiOH}$



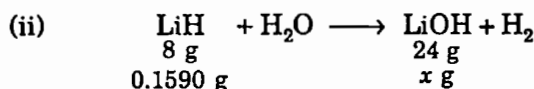
There observations are confirmed quantitatively.



$$\frac{14}{30} = \frac{0.347}{0.747}$$

$$0.467 = 0.464 \quad (\text{very approximately equal})$$

hence Li.



equivalent of LiOH = equivalent of HCl

$$= \frac{200 \times 0.1}{1000} = 0.02$$

$$0.02 \text{ equivalent of LiOH} = 0.48 \text{ g}$$

$$\text{Thus,} \quad \frac{8}{0.1590} = \frac{24}{x}$$

$$\Rightarrow x = 0.477 \text{ g} \approx 0.48 \text{ g}$$

which also confirms (A) is Li.

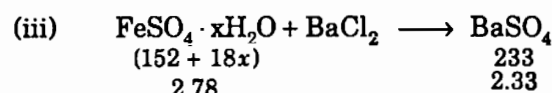
7. By (iii), it is clear that (A) has  $\text{SO}_4^{2-}$

(A) decolourises  $\text{MnO}_4^-/\text{H}^+$

(A) turns  $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$  green

$\Rightarrow$  (A) has  $\text{Fe}^{2+}$

$\Rightarrow$  (A) is  $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$

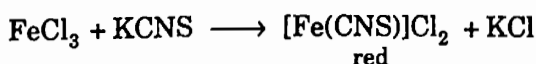
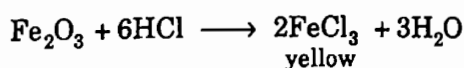
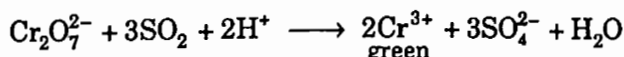
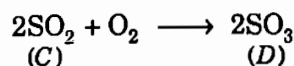
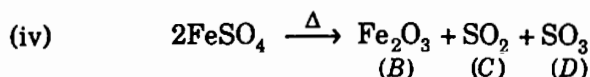
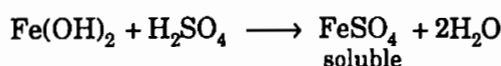
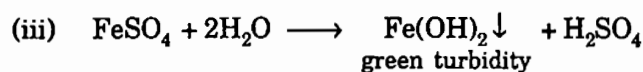
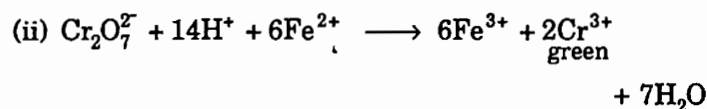
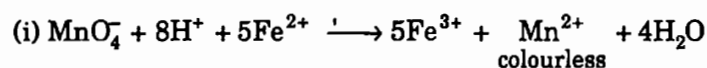


$$\frac{152 + 18x}{233} = \frac{2.78}{2.33}$$

$$\Rightarrow x = 7$$

$\Rightarrow$  (A) is  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

**Explanation :**



## Passage Comprehension Questions

### Passage 1

1. (d) 2. (a) 3. (c) 4. (b) 5. (c) 6. (d)

### Passage 2

1. (a) 2. (b)

### Passage 3

1. (a) 2. (b) 3. (d) 4. (c) 5. (a)

### Passage 4

1. (c) 2. (b) 3. (a) 4. (c)

### Passage 5

1. (c) 2. (b) 3. (a) 4. (b) 5. (d) 6. (b)  
7. (a)

### Passage 6

1. (c) 2. (a) 3. (b) 4. (a)

### Passage 7

1. (b) 2. (a)

### Passage 8

1. (b) 2. (a) 3. (a)

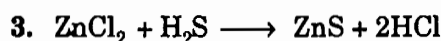
## Assertion & Reason

1. (e) 2. (a) 3. (b) 4. (c) 5. (b) 6. (c)  
7. (d) 8. (a) 9. (d) 10. (a)

## True & False

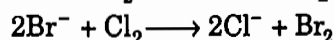
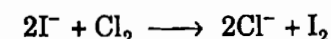
1.  $\text{NH}_4\text{Cl}$  is used alongwith  $\text{NH}_4\text{OH}$  in group III to decrease ionisation of  $\text{NH}_4\text{OH}$  by common-ion effect (of  $\text{NH}_4^+$ ).  $(\text{NH}_4)_2\text{SO}_4$  is also a source of  $\text{NH}_4^+$  ion but it can't be used since  $\text{SO}_4^{2-}$  ion will precipitate  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  ions as their sulphate; hence **false**.

2.  $\text{HCl}$  (common  $\text{H}^+$  ion) decreases ionisation of  $\text{H}_2\text{S}$  giving less  $[\text{S}^{2-}]$  that can precipitate group II as sulphides. But  $\text{H}_2\text{SO}_4$ , although a good source of  $\text{H}^+$ , will precipitate  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  etc. as their sulphates, hence **false**.



$\text{ZnS}$  is formed but remains soluble due to formation of  $\text{HCl}$ .  $\text{ZnS}$  is precipitated when  $\text{H}_2\text{S}$  is passed in ammoniacal medium, hence **false**.

4. Reducing power of  $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$



Thus,  $\text{I}_2$  is formed in preference of  $\text{Br}_2$ , and gives violet colour in  $\text{CHCl}_3$ , hence **true**.



$\text{AB}$  is precipitated if  $[\text{A}^+][\text{B}^-] > K_{\text{sp}}$

$\text{AgCl}$  is precipitated if  $[\text{Ag}^+][\text{Cl}^-] > K_{\text{sp}}$

$\text{PbI}_2$  is precipitate of  $[\text{Pb}^{2+}][\text{I}^-]^2 > K_{\text{sp}}$ , hence **true**.

6.  $M(OH)_3$  is precipitated

$$[M^{3+}][OH^-]^3 > K_{sp}$$

$$[OH^-] > 1 \times 10^{-3}$$

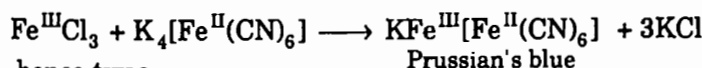
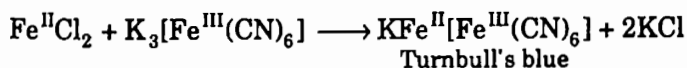
$$[OH^-] > 1 \times 10^{-3}$$

maximum  $pOH = 3$

maximum  $pH = 9$

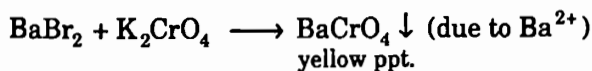
hence true.

7. Turnbull's blue colour is obtained when  $Fe^{2+}$  salts react with  $K_3[Fe^{III}(CN)_6]$  and Prussian's blue colour is obtained when  $Fe^{3+}$  salts react with  $K_4[Fe^{II}(CN)_6]$ .



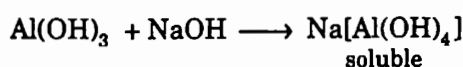
hence true.

8.  $BaBr_2 + AgNO_3 \longrightarrow AgBr \downarrow$  (due to  $Br^-$ )  
yellow ppt.



hence true.

9.  $AlCl_3 + NaOH \longrightarrow 3NaCl + Al(OH)_3 \downarrow$



hence true.

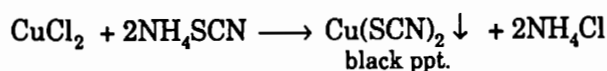
10.  $Fe(OH)_3$  is insoluble while  $Al(OH)_3$  is soluble in  $NaOH$  forming  $NaAlO_2$  or  $Na[Al(OH)_4]$

hence true.

11.  $SnS$  and  $As_2S_3$  both are soluble in YAS,

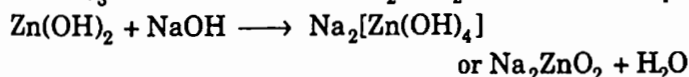
hence false.

12.  $CoCl_2 + 4NH_4SCN \longrightarrow (NH_4)_2[Co(SCN)_4] + 2NH_4Cl$   
blue colour



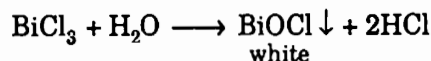
hence true.

13.  $NaOH$  can dissolve both  $Al(OH)_3$  and  $Zn(OH)_2$



hence false.

14.  $SbCl_3 + H_2O \longrightarrow SbOCl \downarrow + 2HCl$   
orange



white turbidity is due to  $BiOCl$  (while orange turbidity is due to  $SbOCl$ )

hence false.

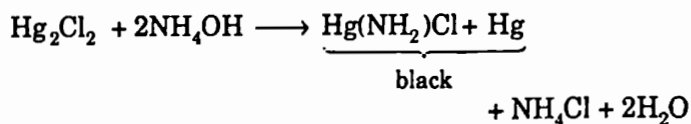
15.  $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$   
(green)

$Cr_2O_7^{2-}/H^+$  can oxidise  $Fe^{2+}$  to  $Fe^{3+}$  giving green colouration at the end point

hence true.

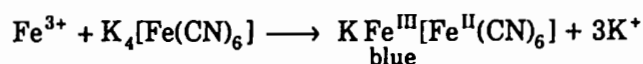
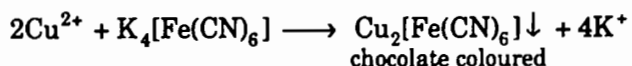
16. White ppt. of  $PbCl_2$  is soluble in hot water hence false.

17. White ppt. of  $Hg_2Cl_2$  is blackened by  $NH_3$  due to formation of  $[Hg(NH_2)Cl + Hg]$



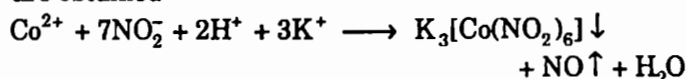
and not by iodide of Millon's base, hence false.

18.  $K_4[Fe(CN)_6]$  gives different coloured ppt. with  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$



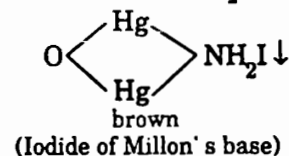
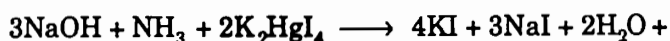
hence true.

19. Yellow ppt. of  $K_3[Co^{III}(NO_2)_6]$  and not of  $K_4[Co(NO_2)_6]$  are obtained



hence false.

20.  $NH_4Cl + NaOH \longrightarrow NH_3 + NaCl + H_2O$



### Fill in the Blanks

- (a) common ion effect (b)  $K_{sp}$  values
- (a) III (b) decrease (c)  $OH^-$  3. (a) dil.  $HCl$  (b)  $H_2S$
- (a) complex formation (b)  $KCN$  (c)  $K_3[Cu(CN)_4]$   
(d)  $K_4[Cd(CN)_4]$  (e)  $CdS$
- (a) hot water (b) aq.  $NH_3$  (c) blackened
- (a) YAS or  $NaOH$  7. (a)  $SbOCl$  (b)  $Sb^{3+}$
- (a)  $NaOH$  (b)  $Al(OH)_3$  (c)  $NaAlO_2$  (d)  $Fe(OH)_3$
- (a)  $H_2O_2$  (b)  $Na_2CrO_4$  (c) yellow (d)  $PbCrO_4$   
(e)  $(CH_3COO)_2Pb$
- (a) dimethyl glyoxime
- (a)  $Fe^{2+}$  (or  $C_2O_4^{2-}$ ,  $SO_2$  etc.)
- (a)  $Fe^{2+}$  (b)  $C_2O_4^{2-}$  13. (a) red
- (a) Turnbull's blue (b)  $K_3[Fe(CN)_6]$  (c) Prussian blue  
(d)  $K_4[Fe(CN)_6]$
- (a)  $K_4[Fe(CN)_6]$
- (a)  $CH_3COONH_4$  (b)  $(CH_3COO)_2Pb$
- (a)  $[Al^{3+}][OH^-]^3$  (b) greater
- (a)  $KI$  (b)  $K_2HgI_4$  (c) Nessler's reagent
- (a)  $Fe^{3+}$  (b)  $[Fe(SCN)]^{2+}$  20. (a)  $SO_2$
- (a)  $H_2S$  22. (a)  $Na_3[Ag(S_2O_3)_2]$

[illegible]

During a total eclipse of the sun on August 18, 1868, spectroscopic examination of the sun's chromosphere led to the discovery of helium, name derived from the Greek word 'helios' meaning sun."

20

## Group 18 (VIIIA—The Noble Gases)

### Discovery

Discovery of the noble gases in the Periodic Table were based on the study of physical properties as spectral behaviour and density. Chemists associated with the discovery of inert gases were

|                          |      |                                                                                                                                                                   |
|--------------------------|------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1. Henry Cavendish       | 1785 | Mixture of noble gases (but could not be identified due to lack of facility of study)                                                                             |
| 2. Lockyer and Frankland | 1868 | Helium (Greek word helios — Sun) based on study of sodium D-lines in spectrum in solar eclipse                                                                    |
| 3. L. Palmieri           | 1881 | As above                                                                                                                                                          |
| 4. Ramsay                | 1895 | Ar (meaning lazy)                                                                                                                                                 |
| 5. Ramsay                | 1896 | Assigned position to He and Ar (in Periodic Table) (zero group being inert). He also predicted that there should be other three inert gases to complete the table |
| 6. Ramsay and Travers    | 1898 | Isolated three new elements by low-temperature distillation of liquid air : neon (Greek-new) krypton (Greek-hidden) xenon (Greek-strange)                         |
| 7. Rutherford and Soddy  | 1902 | Isolated radon (Latin word radius—ray)                                                                                                                            |

In 1904 Nobel Prize in physics was awarded to Lord Rayleigh for investigation on gas densities and for discovery of argon, Nobel Prize in Chemistry was awarded to W. Ramsay for discovery of the inert gas elements in air and their place in the periodic system.

### Learning Framework of the Chapter

- Discovery
- Isolation of the Elements
- Position of Noble Gases in the Periodic Table
- Periodic Properties
- Study of Compounds of Group 18
- Structure of Xenon Compounds

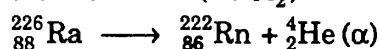
|                  |
|------------------|
| $^2\text{He}$    |
| $^{10}\text{Ne}$ |
| $^{18}\text{Ar}$ |
| $^{36}\text{Kr}$ |
| $^{54}\text{Xe}$ |
| $^{86}\text{Rn}$ |

## Isolation of the Elements

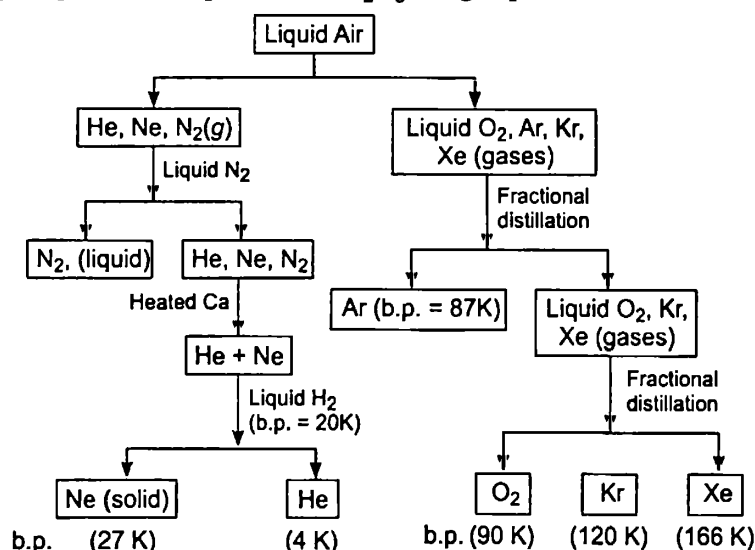
- Main source of helium is natural gas. The hydrocarbons are liquefied at about 120 K and helium is pumped out.
- Liquid air is subjected to fractional distillation to isolate Ne, Ar, Kr and Xe. Separation depends on the boiling points.

| Gas            | Boiling points/K |
|----------------|------------------|
| He             | 4                |
| Ne             | 27               |
| Ar             | 87               |
| Kr             | 120              |
| Xe             | 166              |
| N <sub>2</sub> | 77               |
| O <sub>2</sub> | 90               |

- Rn (Radon) is produced by the  $\alpha$ -decay of an aqueous solution of radium chloride (RaCl<sub>2</sub>)



The gas is mainly diluted by ozone, hydrogen and oxygen (obtained by the  $\alpha$ -irradiation of water). The mixture of gases is passed successively over heated copper and copper (II) oxide [Cu + CuO] and finally dried with phosphorus (V) pentoxide [P<sub>2</sub>O<sub>5</sub>] to get pure radon.



## Position of Noble Gases in the Periodic Table

| Group 17                        | Group 18                                       | Group 1                     |
|---------------------------------|------------------------------------------------|-----------------------------|
| Most electronegative            | Inert                                          | Most electropositive        |
| Halogen                         | He <sub>2</sub>                                | Li <sub>3</sub>             |
| F <sub>9</sub>                  | Ne <sub>10</sub>                               | Na <sub>11</sub>            |
| Cl <sub>17</sub>                | Ar <sub>18</sub>                               | K <sub>19</sub>             |
| Br <sub>35</sub>                | Kr <sub>36</sub>                               | Rb <sub>37</sub>            |
| I <sub>53</sub>                 | Xe <sub>54</sub>                               | Cs <sub>55</sub>            |
| At <sub>85</sub>                | Rn <sub>86</sub>                               | Fr <sub>87</sub>            |
| ns <sup>2</sup> np <sup>5</sup> | ns <sup>2</sup> np <sup>6</sup><br>(except He) | [Inert gas] ns <sup>1</sup> |

In Mendeleev's original Periodic Table there was a sharp transition from strongly electronegative elements of Group 17 (VIIA — halogen family) to the strongly electropositive elements of Group 1 (IA — alkali metals). It was suggested by Thomson that there should be a group between Group 17 and Group 1 which can make a smooth transition. When Ar and He were discovered they could be placed in this group easily. This was called zero group as the elements were found to be chemically inert and hence they may be assumed to have zero valency. Subsequently when neon, krypton, xenon and radon were discovered, they fitted excellently with helium and argon in the same group.

They have electronic configuration  $ns^2np^6$  of the valence shell (except helium —  $1s^2$ ) with complete octet in which the electrons are all paired. This accounts for the remarkable stability of these gases and lack of chemical activity compared to other elements of the Periodic Table. According to the latest IUPAC convention, number 18 has been assigned to this group.

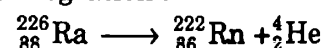
Molecular weight (by vapour density method) is same as atomic weight thus these are monoatomic gases.

Also, 
$$\frac{C_p}{C_v} = 1.667$$

which confirmed that they are monoatomic gases ( $C_p$  is the molar heat capacity at constant pressure and  $C_v$  is the molar heat capacity of constant volume).

## Periodic Properties

- Because of highest ionisation energy of group 18 elements in their respective periods, they were given the name '**noble gases**' and thus inert. However, at least in the case of xenon, it is not so; it forms series of compounds.
- The noble gases are low boiling gases. Except for radon (Rn), they can be isolated by fractional distillation of liquefied air. Rn is collected from the radioactive disintegration:



- All isotopes of radon are radioactive and there is concern in the some areas of the world where poor ventilations in homes result in build-up of radon gas (which comes from the rocks upon which homes are built).

## DEEP Focus

- The noble gases are colourless, tasteless and odourless. In the liquid and solid states the only forces of attraction among the atoms are **very weak London or van der Waals' forces**. **Polarisability** and interatomic interactions increase with increasing atomic number. The attractive forces among the atoms are so small that the remain liquid at 1 atmospheric pressure even at a temperature of 0.001 K.

- Physical properties of Group 18 (the noble gases) have been summarised in Table 20.1 and Fig. 20.1
- Helium was first detected as a new element in the spectrum of the sun in 1868 (hence, its name is connected with helios, the Greek word for sun). Radon was discovered as the product of the radioactive decay of uranium and thorium.

### DEEP Focus

- Helium has the lowest boiling point of any element, and its behaviour as a liquid is most unusual. It has no triple point that is there is no single combination of temperature and pressure at which the solid, the liquid and the gas all exist. **At about 2K**, helium undergoes a transition to a form of helium, labelled  $\text{He}_{\text{II}}$ . It will creep up the walls of the container in which it is placed and thus it exists in **two phases in liquid helium, one of which has an extremely low viscosity**. Uses have been summarised in Table 20.3

Table 20.1 Physical Properties of Group 18 Element

| Property                                                     | He                               | Ne                               | Ar                          | Kr                              | Xe                              | Rn                                      |
|--------------------------------------------------------------|----------------------------------|----------------------------------|-----------------------------|---------------------------------|---------------------------------|-----------------------------------------|
| Atomic number                                                | 2                                | 10                               | 18                          | 36                              | 54                              | 86                                      |
| Electronic configuration                                     | $1s^2$                           | $[\text{He}] 2s^2 2p^6$          | $[\text{Ne}] 3s^2 3p^6$     | $[\text{Ar}] 3d^{10} 4s^2 4p^6$ | $[\text{Kr}] 4d^{10} 5s^2 5p^6$ | $[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^6$ |
| ( $I_1$ )/kJ mol <sup>-1</sup>                               | 2372                             | 2080                             | 1521                        | 1351                            | 1170                            | 1040                                    |
| Melting point/°C                                             | —                                | -248.6                           | -189.4                      | -157.2                          | -111.8                          | -71                                     |
| Boiling point/°C                                             | -269                             | -246                             | -186                        | -153.6                          | -108.1                          | -62                                     |
| Atomic radius/pm                                             | 120                              | 160                              | 191                         | 200                             | 220                             | —                                       |
| Density at STP/ g/cm <sup>3</sup>                            | $1.8 \times 10^{-4}$             | $9.0 \times 10^{-4}$             | $1.8 \times 10^{-3}$        | $3.7 \times 10^{-3}$            | $5.9 \times 10^{-3}$            | $9.7 \times 10^{-3}$                    |
| Atmospheric content/% by volume                              | $5.24 \times 10^{-4}$            | $1.82 \times 10^{-3}$            | 0.934                       | $1.14 \times 10^{-3}$           | $8.7 \times 10^{-6}$            | —                                       |
| Principal oxidation no.                                      | 0                                | 0                                | 0                           | 0                               | +2, +4, +6                      | 0                                       |
| Enthalpy of vaporisation/kJ mol <sup>-1</sup>                | 0.08                             | 1.7                              | 6.5                         | 9.1                             | 12.7                            | 18.1                                    |
| Solubility in water at 20°C/cm <sup>3</sup> kg <sup>-1</sup> | 8.61                             | 10.5                             | 33.6                        | 59.4                            | 108.1                           | 230                                     |
| Discovery                                                    | 1895<br>Sir William Ramsay (SWR) | 1898<br>SWR & M.W. Travers (MWT) | 1894<br>SWR & Lord Rayleigh | 1898<br>SWR & MWT               | 1898<br>SWR & MWT               | 1902<br>Friedrich Dorn                  |
| Abundance in igneous rocks/ppm by weight                     | $3 \times 10^{-3}$               | $7 \times 10^{-5}$               | $4 \times 10^{-2}$          | —                               | —                               | $1.7 \times 10^{-10}$                   |

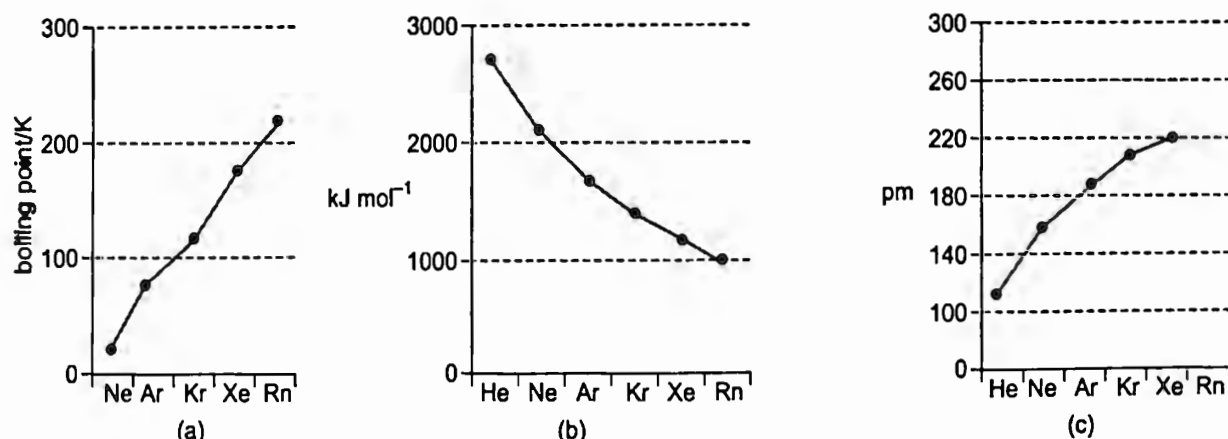


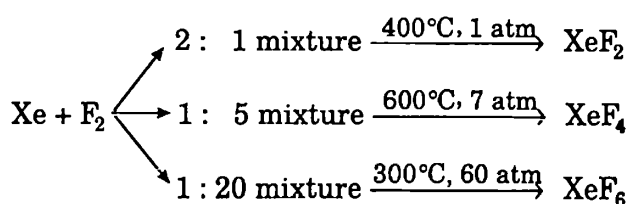
Fig. 20.1 Some group trends of the group 18 elements (a) Boiling point, (b) The first ionisation energy and (c) Atomic radius.

## Study of Compounds of Group 18

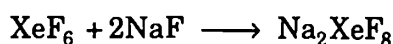
- The noble gases were isolated and discovered because of their lack of reactivity. For a long time it was thought that they really were chemically inert. Before 1962, the only evidence for compound formation by the noble gases was some **molecular ions** formed in discharge tube and **clathrate** compounds.
- Several molecular ions such as  $\text{He}_2^+$ ,  $\text{HeH}^+$ ,  $\text{HeH}_2^+$  and  $\text{Ar}^{2+}$  are formed under high energy conditions in discharge tubes.
- If an aqueous solution of quinol is crystallised under a pressure of 10–40 atm of Ar, Kr, or Xe, the gas becomes trapped in the cavities of about 4 Å diameter in the  $\beta$ -quinol structure. These are called **clathrate compounds**. They do not form bonds in the cavities. When the clathrate is dissolved, the hydrogen bonded arrangement of  $\beta$ -quinol breaks down and the noble gas escapes. The smaller noble gases He and Ne do not form clathrate compounds because the gas atoms are small enough to escape from the cavities. Clathrate provides a convenient means of storing radioactive isotopes of Kr and Xe produced in nuclear reactors.

### Xenon Fluorides

- Xenon reacts directly with fluorine when the gases are heated at 300–600°C in a sealed nickel vessel, and the products formed depend on the Xe/F<sub>2</sub> ratio.

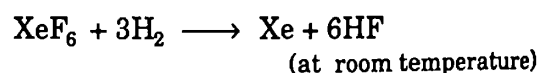
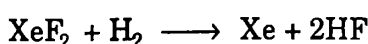


- These conversions are usually quantitative under the given conditions.  $\text{XeF}_6$  may be completely separated from  $\text{XeF}_2$  and  $\text{XeF}_4$  by passing over dry NaF when  $\text{XeF}_6$  alone is absorbed.

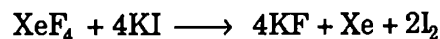
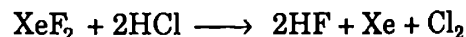


The complex decomposes on heating to give  $\text{XeF}_6$

- These are colourless (white) volatile solids.  $\text{XeF}_6$  is yellow in the liquid and gaseous phases. The fluorides form large crystals on standing in closed vessels.  $\text{XeF}_2$  and  $\text{XeF}_4$  can be handled conveniently in glass vacuum system but  **$\text{XeF}_6$  attacks glass or quartz**. They can be sublimed at room temperature, and can be stored indefinitely in nickel or monel (an alloy of nickel) containers.
- $\text{H}_2$  reduces xenon fluorides to Xe :

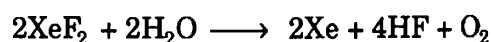


- Xenon fluorides oxidise  $\text{Cl}^-$  to  $\text{Cl}_2$  and  $\text{I}^-$  to  $\text{I}_2$  :  
Oxidising power increase in the order :

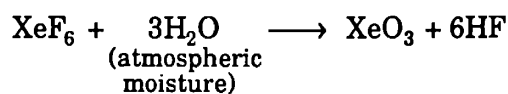
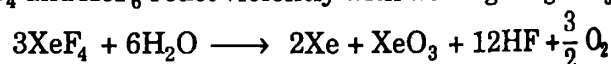


This reaction is used to estimate  $\text{XeF}_4$ .  $\text{I}_2$  formed is titrated using Hypo.

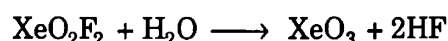
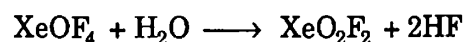
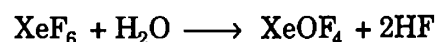
- They also oxidise  $\text{Ce}^{3+}$  salts to  $\text{Ce}^{4+}$  salts.
- $\text{XeF}_2$  is soluble in water but undergoes slow hydrolysis :



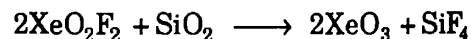
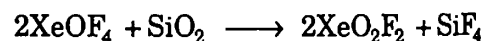
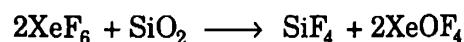
- $\text{XeF}_4$  and  $\text{XeF}_6$  react violently with water giving  $\text{XeO}_3$  :



This takes place in three stages :



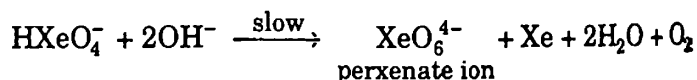
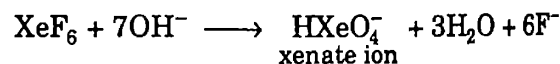
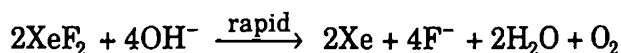
- $\text{SiO}_2$  also converts  $\text{XeF}_6$  into  $\text{XeOF}_4$  :



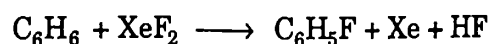
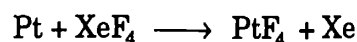
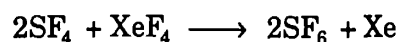
$\text{SiO}_2$  is part of glass or quartz. Hence,  $\text{XeF}_6$  cannot be stored in glass or quartz vessel.

Here  $\text{XeF}_6$  behaves as an acid (oxide ion acceptor) according to Lux–Flood definition.

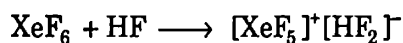
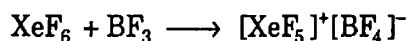
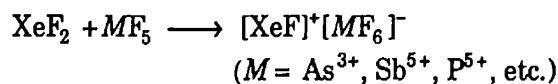
- They are also hydrolysed in alkaline solution rapidly :



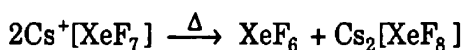
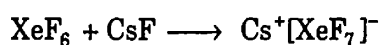
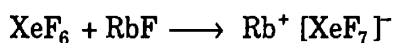
- They are also used as fluorinating agent :



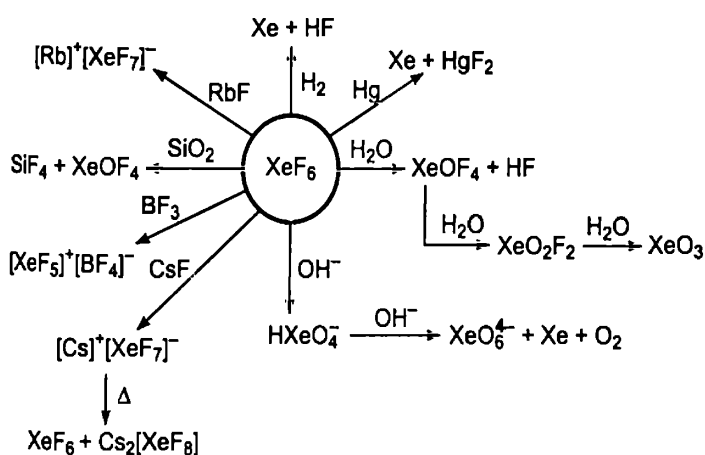
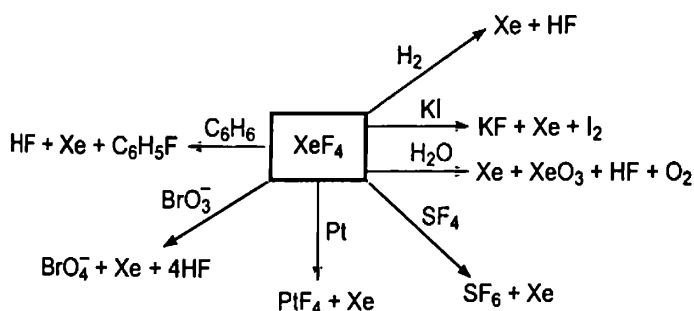
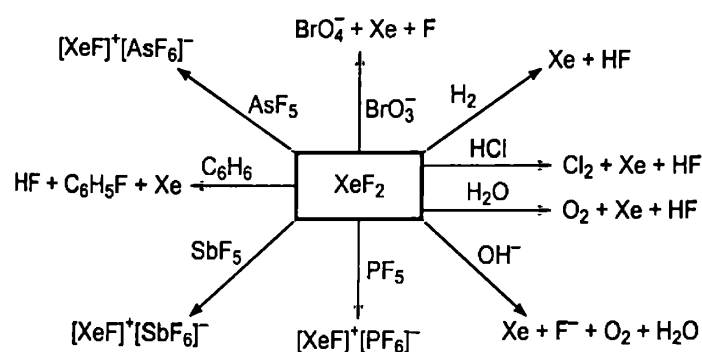
- Xenon fluorides act as fluoride donor and forms complexes which are conducting due to formation of ions:



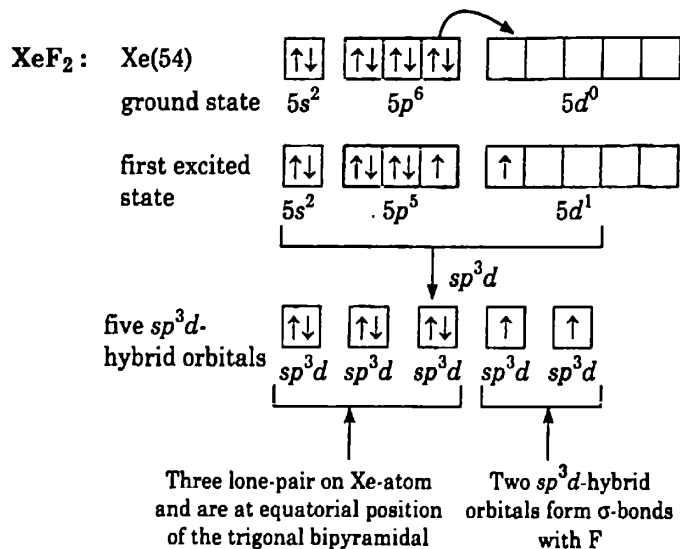
$\text{XeF}_6$  may also act as a fluoride acceptor:



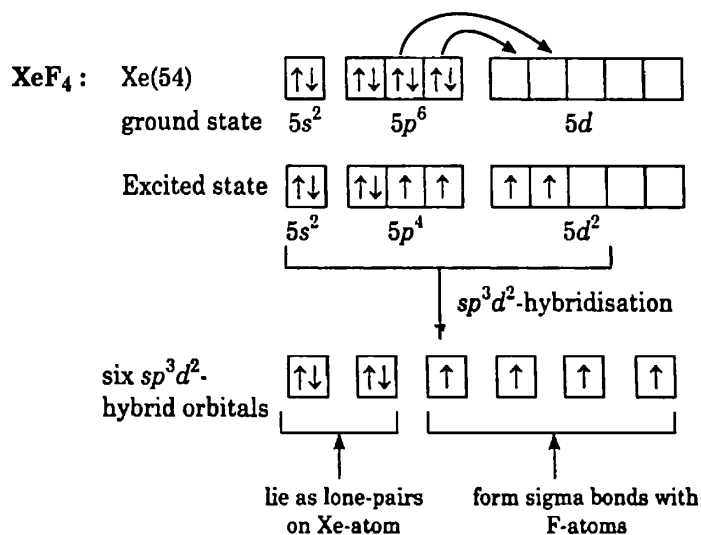
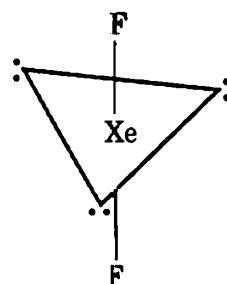
Structure of xenon fluorides are summarised in Table 20.3.



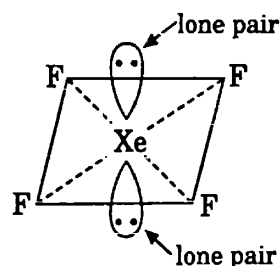
## Structure of Xenon Compounds



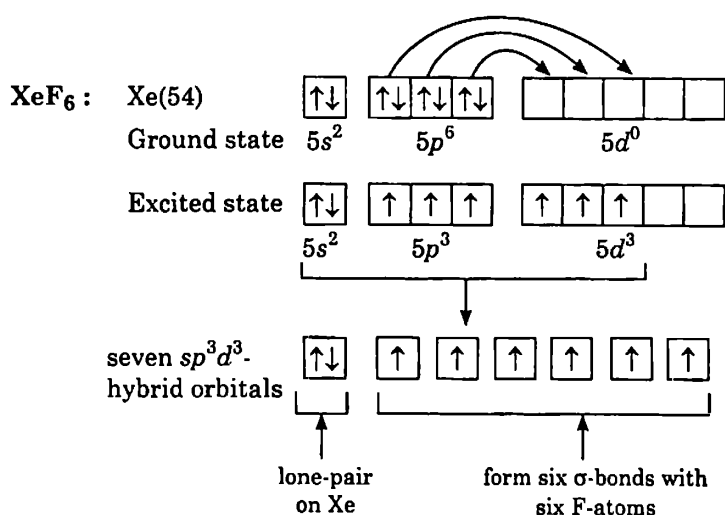
Thus, structure is linear



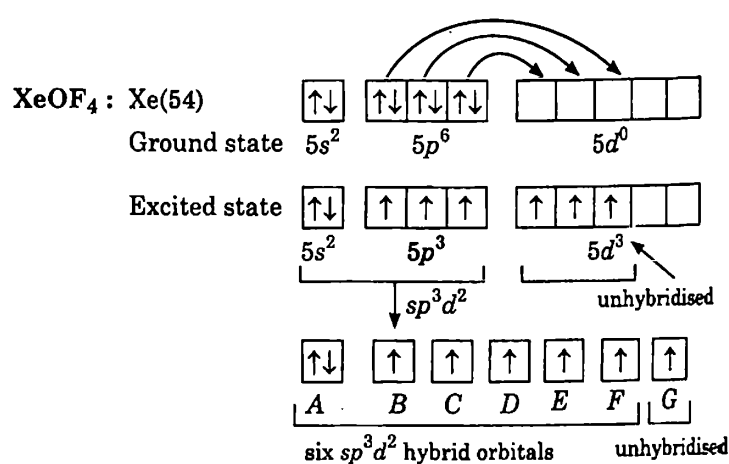
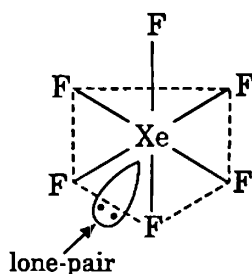
Thus,  $\text{XeF}_4$  assumes square planar structure.







Structure is distorted octahedron



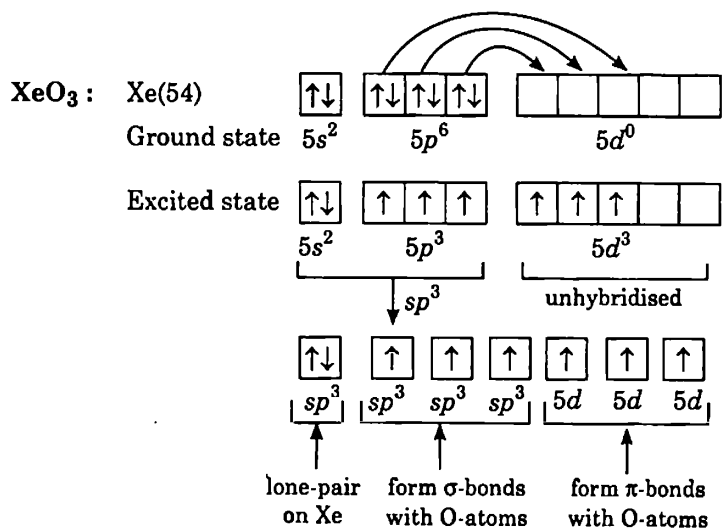
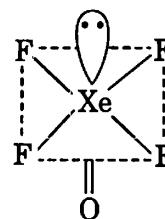
A — lone-pair on Xe

B to E — form four  $\sigma$ -bonds with four F-atoms

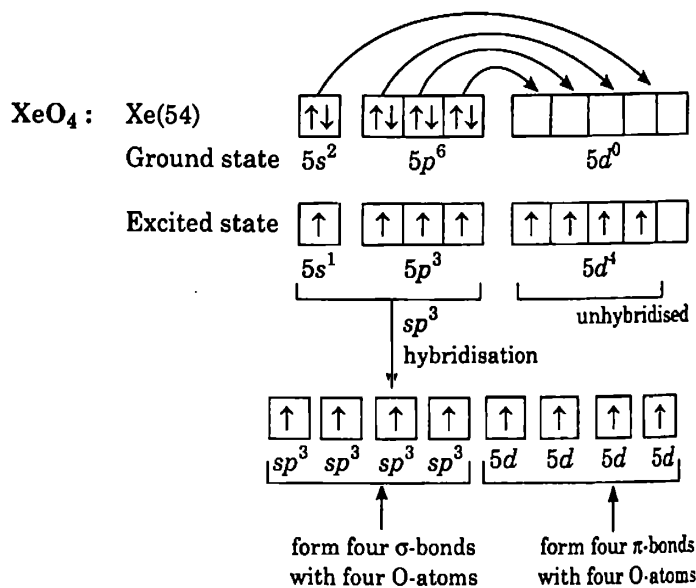
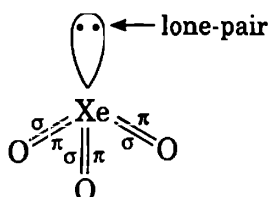
F — forms  $\sigma$ -bond with O-atom

G — forms  $\pi$ -bond with O-atom

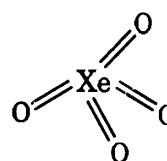
Structure is square pyramidal



Due to lone pair-bond pair repulsion XeO<sub>3</sub> assumes trigonal pyramidal structure (instead of tetrahedral structure —  $sp^3$  hybridisation) and bond angle is  $103^\circ$  (VSEPR Theory)



Structure is tetrahedral



Structure have been summarised in Table 20.2

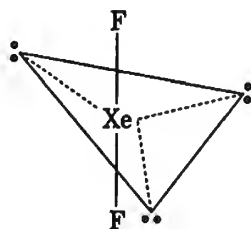
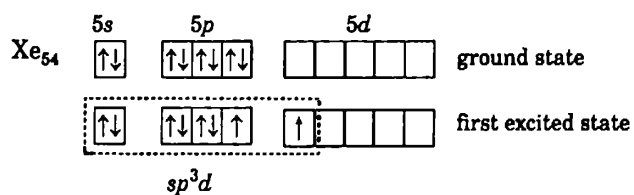
Table 20.2 Structures of Some Xenon Compounds

| Formula                              | (M.p.)°C | Oxidation state | Number of     |            | Hybridisation of Xe | Structure                                                     | Form                  |
|--------------------------------------|----------|-----------------|---------------|------------|---------------------|---------------------------------------------------------------|-----------------------|
|                                      |          |                 | bonding pairs | lone pairs |                     |                                                               |                       |
| XeF <sub>2</sub>                     | 129      | +2              | 2             | 3          | $sp^3d$             | linear with three lone pairs in equatorial position.          |                       |
| XeF <sub>2</sub> · 2SbF <sub>3</sub> | 63       | —               | —             | —          | —                   | —                                                             | yellow solid crystals |
| XeF <sub>4</sub>                     | 117      | +4              | 4             | 2          | $sp^3d^2$           | square planar with two positions occupied by lone pairs.      | colourless crystals   |
| XeOF <sub>2</sub>                    | 31       | +4              | 4             | 2          | $sp^3d$             | T-shaped                                                      | colourless crystals   |
| XeF <sub>6</sub>                     | 49.6     | +6              | 6             | 1          | $sp^3d^3$           | distorted octahedron.                                         | colourless crystals   |
| XeO <sub>3</sub>                     | —        | +6              | 6             | 1          | $sp^3$              | trigonal pyramidal with three $\pi$ -bonds and one lone pair. | colourless liquid     |
| XeO <sub>2</sub> F <sub>2</sub>      | —        | +6              | 6             | 1          | $sp^3d^2$           | trigonal pyramidal with two $\pi$ -bonds and one lone pair.   | colourless liquid     |
| XeOF <sub>4</sub>                    | 46       | +6              | 6             | 1          | $sp^3d^2$           | square pyramidal with one $\pi$ -bond and one lone pair.      | colourless crystals   |
| XeO <sub>4</sub>                     | —        | +8              | 4             | 0          | $sp^3$              | tetrahedral                                                   | colourless gas        |
| XeO <sub>6</sub> <sup>4-</sup>       | —        | +8              | 4             | 0          | $sp^3d^2$           | octahedral                                                    | ions                  |

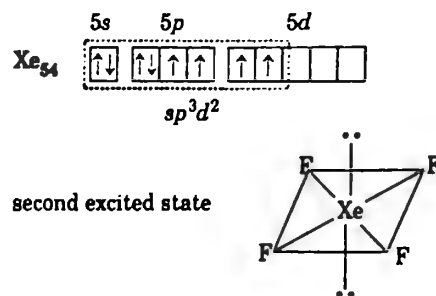
Table 20.3 Uses of the Noble Gases

| Noble gas | Use                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | Reasons                                                                                                                                                                                                                                                                                                                                                             |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Helium    | <ol style="list-style-type: none"> <li>1. Filling of observation balloons and other lighter-than-air craft</li> <li>2. He/O<sub>2</sub> mixture for deep-sea breathing, instead of N<sub>2</sub>/O<sub>2</sub> mixture</li> <li>3. Diluent for gaseous anaesthetics</li> <li>4. He/O<sub>2</sub> mixtures for respiratory patients</li> <li>5. Heat transfer medium for nuclear reactions</li> <li>6. Liquid He to maintain very low temperature in research (cryogenics)</li> </ol> | <p>Non-flammable; 93% lifting power as compared to flammable H<sub>2</sub></p> <p>Low solubility in blood; prevents nitrogen narcosis and "bends"</p> <p>Nonflammable, non-reactive</p> <p>Low density flows easily through restricted passages</p> <p>Transfers heat readily; does not become radioactive; chemically inert</p> <p>Extremely low boiling point</p> |
| Neon      | Neon signs                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | Even at low Ne pressure, moderate electric current causes bright orange-red glow; can be modified by coloured glass or mixing with Ar or Hg vapour.                                                                                                                                                                                                                 |
| Argon     | <ol style="list-style-type: none"> <li>1. Inert atmosphere for welding</li> <li>2. Filling incandescent light bulbs</li> </ol>                                                                                                                                                                                                                                                                                                                                                       | <p>Chemically inert</p> <p>Inert; prevents vaporisation of tungsten and blackening of bulbs</p>                                                                                                                                                                                                                                                                     |
| Krypton   | Airport runway and approach lights                                                                                                                                                                                                                                                                                                                                                                                                                                                   | Gives longer life to incandescent lights than Ar, but more expensive                                                                                                                                                                                                                                                                                                |
| Xenon     | Xe and Kr mixture in high-intensity, short-exposure photographic flash tubes                                                                                                                                                                                                                                                                                                                                                                                                         | Both have fast response to electric current                                                                                                                                                                                                                                                                                                                         |
| Radon     | Radiotherapy of cancerous-tissues                                                                                                                                                                                                                                                                                                                                                                                                                                                    | Radioactive                                                                                                                                                                                                                                                                                                                                                         |

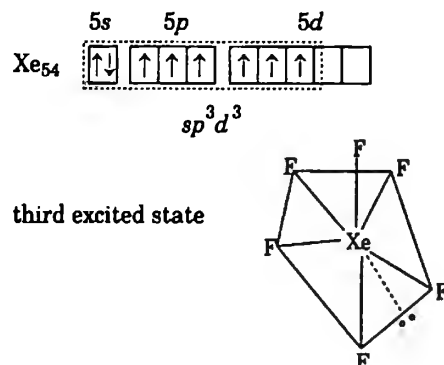




- (b)  $\text{XeF}_4$  : Four unpaired electrons form four  $\sigma$ -bonds with fluorine atoms and two lone-pairs are above and below the plane containing Xe and F atoms. The structure is square planar.



- (c)  $\text{XeF}_6$  : Six unpaired electrons form  $\sigma$ -bonds with F-atoms and one lone-pair at one corner in the distorted octahedron.



6. (a)  $\text{XeF}_4$  (b)  $\text{XeF}_2$  (c)  $\text{XeO}_3$ .

# Total Practice Set

## (Read, Plan & Solve!)

**Problem 1.** A 55 L cylinder contains Ar at 137 atm and 23°C. What minimum volume of air at STP must have been liquefied and distilled to produce this Ar? Air contains 0.934% Ar by volume.

**Solution** moles of pure Ar =  $\frac{pV}{RT} = \frac{137 \times 55}{0.0821 \times 296}$   
 $= 310.062 \text{ mol}$

Since, at STP 1 mol occupies 22.4 L

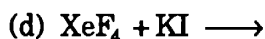
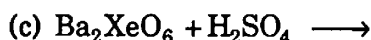
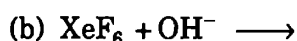
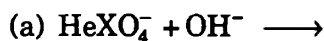
$$\text{Volume of Ar at STP} = 6945.386 \text{ L}$$

Volume of air to have this volume of argon

$$= \frac{6945.386}{0.934} \times 100$$

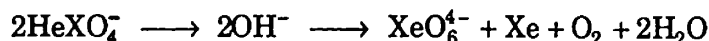
$$= 743617.37 \text{ L}$$

**Problem 2.** Complete the following reactions.

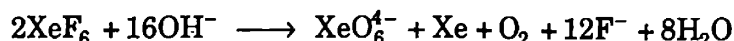


followed by reaction with  $\text{Na}_2\text{S}_2\text{O}_3$

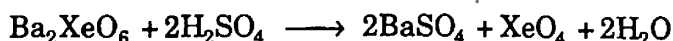
**Solution** (a)  $\text{HXeO}_4$  (xenate) slowly disproportionates in alkaline solution to form  $\text{XeO}_6^{2-}$  (perxenate) and Xe



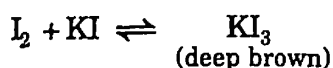
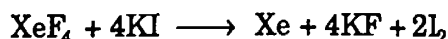
(b) Alkaline hydrolysis of  $\text{XeF}_6$  gives perxenates



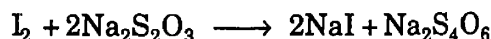
(c)  $\text{BaSO}_4$  is precipitated and  $\text{XeO}_4$  (explosive) is formed



(d) KI is oxidised to  $\text{I}_2$  (and exists as  $\text{KI}_3$ )

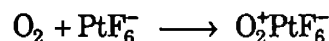
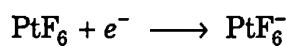
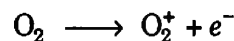


Liberated  $\text{I}_2$  can be estimated by  $\text{Na}_2\text{S}_2\text{O}_3$



**Problem 3.** Bartlett observed that  $\text{PtF}_6$  changes colour on exposure to air. What conclusion is drawn regarding formation of Xe compounds?

**Solution** Bartlett observed that  $\text{PtF}_6$  changes colour on exposure to air. Investigation concluded that  $\text{PtF}_6$  is a very strong oxidising agent that can oxidise  $\text{O}_2$  to  $\text{O}_2^+$  and thus orange colour compound  $\text{O}_2^+\text{PtF}_6^-$  is formed.

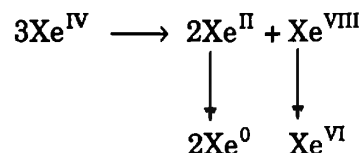


Ionisation energy of Xe = 1169 kJ mol<sup>-1</sup>

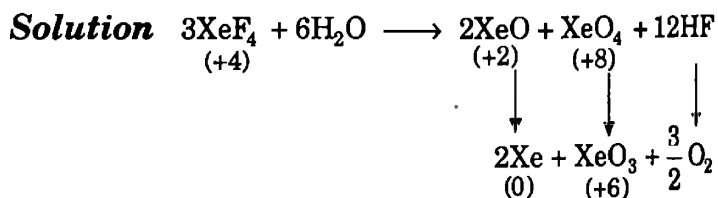
Ionisation energy of  $\text{O}_2$  = 1175 kJ mol<sup>-1</sup>

Since, ionisation energies of  $\text{O}_2$  and Xe are very equal, thus oxidation of Xe by  $\text{PtF}_6$  would also be possible. Bartlett also isolated a compound  $\text{Xe}^+\text{PtF}_6^-$  (orange). Later stage gave so many compounds of Xe

**Problem 4.**  $\text{Xe}^{\text{IV}}$  disproportionates to  $\text{Xe}^0$  and  $\text{Xe}^{\text{VI}}$  through  $\text{Xe}^{\text{II}}$  and  $\text{Xe}^{\text{VIII}}$



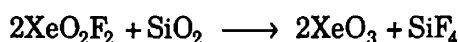
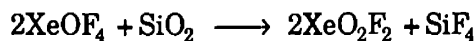
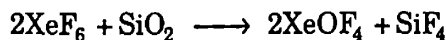
Explain disproportionation of  $\text{XeF}_4$  by  $\text{H}_2\text{O}$ .



## Explanation

(a)  $\text{XeF}_6$  cannot be stored in a vessel made of glass or quartz.

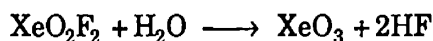
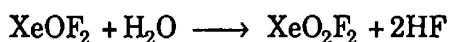
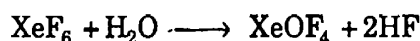
- $\text{XeF}_6$  produces an explosive  $\text{XeO}_3$  on reaction with silica present in glass or quartz



Thus,  $\text{XeF}_6$  cannot be handled in a vessel made of quartz or glass.

(b)  $\text{XeF}_6$  should be stored in a vessel free of moisture

- $\text{XeF}_6$  is hydrolysed to  $\text{XeO}_3$  (end product) which is very difficult to handle due to its explosive nature.



Hence,  $\text{XeF}_6$  should be stored in moisture-free vessel.

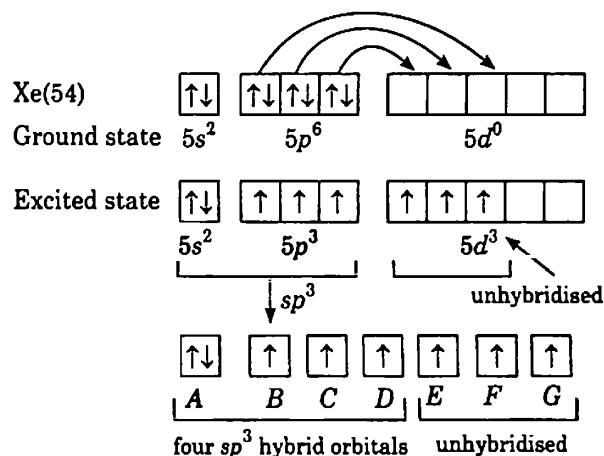
(c) Oxidising power of fluorides of Xe is in order



- Greater the oxidation number of the central element, greater the tendency to be reduced to minimum state hence greater the oxidising power.

| Fluorides      | Oxidation number of Xe | Change in oxidation number if reduced to $\text{Xe(O)}$ | Oxidising power |
|----------------|------------------------|---------------------------------------------------------|-----------------|
| $\text{XeF}_2$ | +2                     | 2 units                                                 | Maximum<br>↓    |
| $\text{XeF}_4$ | +4                     | 4 units                                                 |                 |
| $\text{XeF}_6$ | +6                     | 6 units                                                 |                 |

(d)  $\text{XeO}_3$  is  $sp^3$ -hybridised in Xe but it has pyramidal structure.



A — lone-pair on Xe

B, C, D — form three  $\sigma$ -bonds with O

E, F, G — form three  $\pi$ -bonds with O

Due to lone-pair there is lone-pair—bond-pair repulsion. Thus, geometry of the molecule is distorted to pyramidal instead of tetrahedral.

# Master Exercises

## Exercise 1 (Stage 1 : Learning)

### Short Answer Type Questions

1. What were the reasons for late discovery of noble gases?
2. What made Lord Rayleigh suspect that there may be an additional element in air?
3. What is the relationship between the boiling point and van der Waals' forces?
4. Why there is a steady increase in boiling point from He to Rn?
5. Why no compounds of He and Ne are known?
6. Why noble gas compounds are formed only with  $O_2$  and  $F_2$ ?

7. Why does the tendency to form clathrates increase down the group?
8. How did the terrestrial helium originate?

### Analytical Questions

1. What are the factors which led Bartlett to think that Xe can be oxidised by  $PtF_6$ ?
2. Would you expect nitrogen to form compound of the type  $N_2^+[PtF_6]$ ? Give reason for your answer (Ionisation potential of  $N_2$  is  $1403 \text{ kJ mol}^{-1}$ )
3. Would you expect radon to form more stable compounds than xenon.

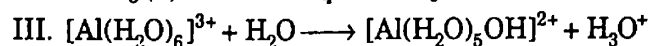
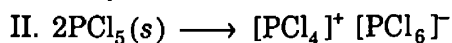
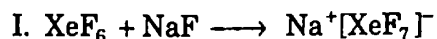
## Exercise 2 (Stage 2 : High Skill Problem Solving)

### Only One Option Correct

1. Consider following properties of the noble gases:  
I : They readily form compounds which are colourless  
II : They generally do not form ionic compounds  
III : They have variable oxidation states in their compounds  
IV : Generally do not form covalent compounds.  
Select correct properties  
(a) I, II, III (b) II, III  
(c) I, III (d) I
2. A rare gas that was detected in the sun before its discovery on earth is  
(a) He (b) Ne  
(c) Ar (d) Kr
3. Which of the following is not known?  
(a)  $XeF_6$  (b)  $XeF_4$   
(c)  $KrF_6$  (d)  $Cs_2XeF_6$

4. End-product of the hydrolysis of  $XeF_6$  is  
(a)  $XeF_4O$  (b)  $XeF_2O_2$   
(c)  $XeO_3$  (d)  $XeO_3^-$
5. When water is allowed to freeze in the presence of Ar, Kr or Xe under pressure then  
(a) atoms of noble gas (G) trapped in the crystal lattice of ice giving clathrates corresponding to the composition  $8G \cdot 26H_2O$   
(b) these are called noble gas hydrates  
(c) both (a) and (b) are correct  
(d) none of the above is correct
6. Select correct statements.  
(a) Helium has the lowest melting point and boiling point  
(b) Helium can diffuse through rubber, PVC and even glass  
(c) Ar, Kr and Xe form clathrate  
(d) All the above are correct statements

7. Consider following transformations

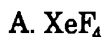


Possible transformations are

- (a) I, II, III                      (b) I, III  
(c) I, II                            (d) II, III

8. Match List I with List II and select the correct answer using the codes given below the list

**List I**



**Codes**

| A     | B | C | D | A     | B | C | D |
|-------|---|---|---|-------|---|---|---|
| (a) 1 | 2 | 3 | 4 | (b) 3 | 1 | 4 | 2 |
| (c) 1 | 3 | 2 | 4 | (d) 2 | 4 | 1 | 3 |

**List II**

1. Distorted octahedral

2. Tetrahedral

3. Square planar

4. Pyramidal

9. Molecule(s) possessing two-centre-two electron bonds and three-centre-four electron bonds would include

- (a)  $\text{B}_2\text{H}_6$  and  $\text{SiF}_4$                       (b)  $\text{XeF}_6$  and  $\text{BF}_6$   
(c)  $\text{B}_2\text{H}_6$  and  $\text{XeF}_6$                       (d)  $\text{B}_2\text{H}_6$  alone

10. Neon lamps are used in botanical gardens and in green houses as they

- (a) provides oxygen  
(b) provide better light  
(c) stimulate growth of plants  
(d) None of the above

11. Which of the following gas mixture is used by the divers inside the sea?

- (a)  $\text{O}_2 + \text{He}$                               (b)  $\text{O}_2 + \text{Xe}$   
(c)  $\text{O}_2 + \text{Ar}$                               (d)  $\text{O}_2 + \text{N}_2$

12. The gas not absorbed by coconut charcoal is

- (a) He                                      (b) Ne  
(c) Ar                                      (d) Kr

13. Which one of the following is square planar?

- (a)  $\text{XeF}_4$                                       (b)  $\text{XeO}_4$   
(c)  $\text{XeO}_3\text{F}$                                       (d)  $\text{XeO}_3\text{F}_2$

14. For advertisement the coloured discharged tubes contain

- (a) He                                      (b) Ne  
(c) Ar                                      (d) Kr

15. The inert gas abundantly found in atmosphere is

- (a) Kr                                      (b) He  
(c) Ar                                      (d) Xe

16. The  $[\text{XeF}]^+$  ions are attached to anion  $[\text{AsF}_6]^-$

- (a) with a linear F-bridge  
(b) with an angular F-bridge  
(c) with H-bond  
(d) with tetrahedral F-bridge

17. Hydrates of helium and neon have not been prepared because of

- (a) low polarisability                      (b) small size  
(c) low boiling point                      (d) all of the above

18. Thermal stability of hydrates of group 18 elements

- (a) increases down the group  
(b) decreases down the group  
(c) remains unchanged  
(d) first increases up to Ar and then decreases

19. Which have distorted geometry based on VSEPR model?

- (a)  $\text{XeF}_2$ ,  $\text{XeF}_4$ ,  $\text{XeO}_3$                       (b)  $\text{XeOF}_2$ ,  $\text{XeO}_3$ ,  $\text{XeF}_2$   
(c)  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}$                       (d) All of these

20. Second most abundant element in the universe (after hydrogen) is

- (a) Al                                      (b) Fe  
(c) He                                      (d) Ne

21. Helium accumulates in the earth's crust through

- (a)  $\alpha$ -decay of radioactive element  
(b) thermonuclear reactions  
(c)  $\beta$ -decay of radioactive element  
(d)  $\gamma$ -decay of radioactive element

22. Most abundant noble gas in air is

- (a) He                                      (b) Ne  
(c) Rn                                      (d) Ar

23. Inert atmosphere for welding of metals is obtained by

- (a) Ar, He                                      (b)  $\text{N}_2$ , He  
(c)  $\text{O}_2$ ,  $\text{N}_2$                                       (d) Ar,  $\text{N}_2$

24. Xenon fluorides acts as fluoride donor with

- (a)  $\text{AsF}_5$                                       (b)  $\text{BF}_3$   
(c) HF                                      (d) all of these

25. Xenon fluoride act as fluoride acceptor with

- (a) RbF                                      (b) CsF  
(c) both (a) and (b)                      (d) None of these

26.  $\text{XeF}_6$  is conducting in presence of

- (a)  $\text{BF}_3$                                       (b) RbF  
(c) HF                                      (d) all of these

27. Which is most basic fluoride?

- (a)  $\text{XeF}_6$   
(b)  $\text{XeF}_2$   
(c)  $\text{XeF}_4$   
(d) None is basic, all are acids

28. Basic character of fluorides increases in the order

- (a)  $\text{XeF}_6 < \text{XeF}_4 < \text{XeF}_2$                       (b)  $\text{XeF}_2 < \text{XeF}_4 < \text{XeF}_6$   
(c)  $\text{XeF}_2 = \text{XeF}_4 < \text{XeF}_6$                       (d)  $\text{XeF}_2 > \text{XeF}_4 < \text{XeF}_6$

29. Which is the best fluorinating agent?

- (a)  $\text{XeF}_2$                                       (b)  $\text{XeF}_4$   
(c)  $\text{XeF}_6$                                       (d)  $\text{XeO}_2\text{F}_2$

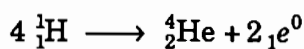
30.  $\text{XeF}_2$  forms ..... with  $\text{AsF}_5$ .

- (a)  $\text{XeF}^+$  cation and  $\text{AsF}_4^+$   
(b)  $\text{XeF}_2^-$  anion and  $\text{AsF}_4^+$   
(c)  $\text{AsF}_4^+$  cation and  $\text{AsF}_4^-$   
(d)  $\text{XeF}^+$  cation and  $\text{AsF}_6^-$  anion



## One or More Than One Options Correct

- Select correct statement(s).
  - The noble gases are present to the extent of about 1% in the earth's atmosphere, the chief component being argon
  - Helium is the second most abundant element in the universe after hydrogen
  - There are two stable isotopes of helium  ${}^3\text{He}$ ,  ${}^4\text{He}$
  - ${}^4\text{He}$  is formed by thermonuclear fusion reaction in stars



- For inert gases  $\frac{C_p}{C_v} = \phi$

- 1.33
- 1.40
- 1.66
- can't be predicted

- Helium is used
  - as a refrigerant (in liquid form) in low-temperature physics
  - as a substituent for nitrogen in the breathing gas for deep-sea divers
  - in radiation therapy
  - in fluorescent tubes

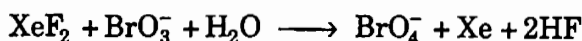
- Select correct statement(s) about  $\text{XeF}_4$ .

- They are thermodynamically stable
- Xe—F bond energy is very high
- They are endothermic compounds
- They are exothermic compounds

- Which practical is/are supposed to be correct?

- Preparation of  $\text{XeF}_6$  in glass or quartz apparatus
- Storing of HF in glass or quartz apparatus
- Storing of  $\text{HNO}_3$  in Al vessel
- Storing of NaOH in Al vessel

- In the following reaction,



- $\text{XeF}_2$  is an oxidising agent
- $\text{XeF}_2$  is a reducing agent
- $\text{BrO}_3^-$  is oxidised to  $\text{BrO}_4^-$
- $\text{XeF}_2$  is reduced to HF

- Select correct statement(s). Bond order of

- $\text{He}_2$  is zero
- $\text{He}_2^+$  is 0.5
- $\text{He}_2^{2+}$  is 1.0
- $\text{Be}_2$  is zero

- Which is/are Lewis acid as well as Lewis base (amphoteric)?

- $\text{XeF}_2$
- $\text{XeF}_4$
- $\text{XeF}_6$
- $\text{XeF}_6^{2-}$

- Oxidising agent(s) is/are

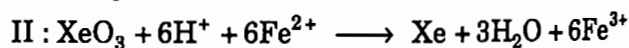
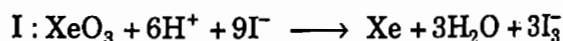
- $\text{XeF}_2$
- $\text{XeF}_4$
- $\text{XeF}_6$
- $\text{XeOF}_4$

- According to the Lux-Flood definition  $\text{XeF}_6$  behaves as
  - an oxidising agent
  - an acid (oxide ion acceptor)
  - a base
  - a reducing agent

## Passage Comprehension Questions

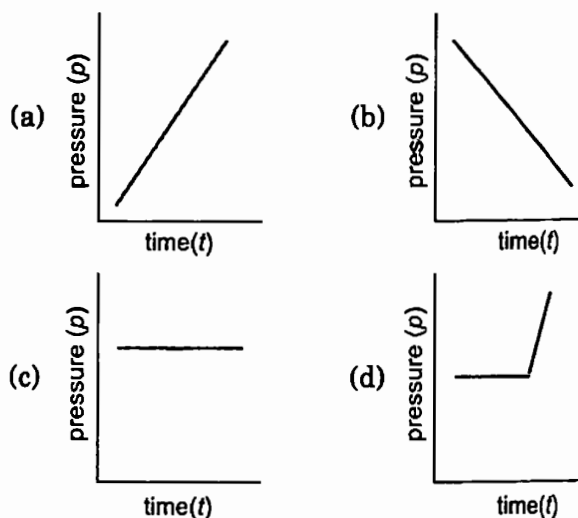
### Passage 1

$\text{XeO}_3$  is an oxidising agent and this can be used to estimate reducing agents.



Answer the following questions

- Reaction can be studied by measuring pressure of the reaction mixture with time variation can be of the type

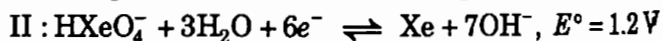
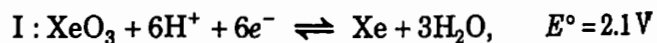


- Select correct statement(s).

- Equivalent of  $\text{XeO}_3$  in I and II is in the ratio 1:1
- Equivalent mass of  $\text{I}_2 = \frac{\text{molar mass}}{9}$
- Equivalent mass of  $\text{Fe}^{2+} = \frac{\text{molar mass}}{6}$
- All the above are correct statements

### Passage 2

$\text{XeO}_3$  is one of the strong oxidising agents in aqueous media :



Answer the following questions

- Which reaction is more spontaneous theoretically?
  - I
  - II
  - Both equally
  - Can't be predicted

2. Select correct statement(s).

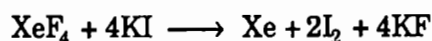
- (a) Equivalent mass of  $\text{XeO}_3 = \frac{\text{molar mass}}{6}$  and  
equivalent mass of  $\text{HXeO}_4^- = \frac{\text{molar mass}}{6}$
- (b) As reaction I or II goes to forward side, pressure increases
- (c) Both are correct statements
- (d) None of the above is correct statement

3. Thermodynamically  $\text{HXeO}_4^-$  should oxidise water, but reaction does not take place. It is due to the fact

- (a) that there is a high activation energy barrier between oxidation state +6 to 0
- (b) that standard emf is positive
- (c) that  $\Delta G^\circ = +ve$
- (d) that  $\Delta G^\circ = -ve$

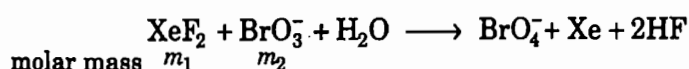
### Passage 3

$\text{XeF}_n$  ( $n = 2, 4, 6$ ) are oxidising agents and thus estimation of Xe salts can be determined by suitable methods.



Based on the above short write up, answer the following questions.

1.  $\text{BrO}_3^-$  is oxidised to  $\text{BrO}_4^-$  by  $\text{XeF}_2$



Ratio of equivalent mass of  $\text{XeF}_2$  and  $\text{BrO}_3^-$  is

- (a)  $\frac{m_1}{m_2}$  (b)  $\frac{2m_1}{m_2}$
- (c)  $\frac{m_1}{2m_2}$  (d)  $\frac{m_1}{3m_2}$

2. Oxidising power increases in the order

- (a)  $\text{XeF}_2 < \text{XeF}_4 < \text{XeF}_6$
- (b)  $\text{XeF}_2 < \text{XeF}_6 < \text{XeF}_4$
- (c)  $\text{XeF}_6 < \text{XeF}_4 < \text{XeF}_2$
- (d)  $\text{XeF}_6 = \text{XeF}_4 = \text{XeF}_2$

3. 1 mole of  $\text{XeF}_4$  on reaction with excess of KI will liberate  $\text{I}_2$  that requires

- (a) 1 mole of  $\text{Na}_2\text{S}_2\text{O}_3$  (b) 2 moles of  $\text{Na}_2\text{S}_2\text{O}_3$
- (c) 0.5 mole of  $\text{Na}_2\text{S}_2\text{O}_3$  (d) 4 moles of  $\text{Na}_2\text{S}_2\text{O}_3$

### Assertion & Reason

Codes :

- (a) Both A and R are true and R is the correct explanation of A.
- (b) Both A and R are true but R is not the correct explanation of A.
- (c) A is true but R is false.
- (d) A is false but R is true.

1. Assertion (A) :  $\text{XeF}_6$  cannot be handled in glass or quartz apparatus.

Reason (R) : Reaction between  $\text{XeF}_6$  and  $\text{SiO}_2$  of glass form explosive  $\text{XeO}_3$ .

2. Assertion (A) : He and Ne do not form clathrates.

Reason (R) : They are difficult to polarise due to smaller size.

3. Assertion (A) : Fluorides of Xe are thermodynamically stable.

Reason (R) : They are endothermic compounds.

4. Assertion (A) :  $\text{XeF}_4$  may be estimated by titrating the  $\text{I}_2$  by reaction with KI.

Reason (R) : Equivalent weight of  $\text{Na}_2\text{S}_2\text{O}_3$  can be determined by iodimetric titration.

5. Assertion (A) :  $\text{XeF}_6$  can be used as an oxidising agent.

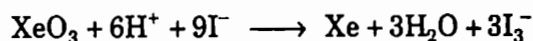
Reason (R) : Oxidation state of Xe in  $\text{XeF}_6$  is +6.

6. Assertion (A) : The reaction  $\text{XeO}_3 + 6\text{H}^+ + 6e^- \rightleftharpoons \text{Xe} + 3\text{H}_2\text{O}$ ,  $E^\circ = 2.1 \text{ V}$

is not feasible thermodynamically to oxidise  $\text{H}_2\text{O}$

Reason (R) : There is a high activation energy barrier between oxidation state +6 and 0 of Xe.

7. Assertion (A) : The reaction,



can be studied kinetically by measurement of pressure.

Reason (R) : Above reaction is called iodometric reaction.

### True & False

- Ionisation energy of  $\text{O}_2$  and Xe are very similar and thus formation of cations  $\text{O}_2^+$  and  $\text{Xe}^+$  is possible.
- $\text{O}_2^+\text{PtF}_6^-$  is an orange-coloured compound.
- In 1904 Nobel Prize in Chemistry was awarded to Lord Rayleigh for investigation on gas densities and for discovery of argon.
- Radon is produced by  $\alpha$ -decay of radium compounds.
- Group 18 elements have been placed in between most electronegative and most electropositive elements.
- $\text{XeF}_6$  can be stored in glass and quartz vessels.
- Xenon fluorides are Lewis acids and Lewis bases.
- $\text{XeF}_4$  disproportionates to stable  $\text{XeO}$  and  $\text{XeO}_4$ .

9. Oxidising power of xenon fluorides increases in the order  $\text{XeF}_6 > \text{XeF}_4 > \text{XeF}_2$ .

10. He and Ne form stable hydrates.

## Fill in the Blanks

- $\text{O}_2^+\text{PtF}_6^-$  (an orange coloured compound) was prepared and thus formation of compound ..... was feasible based on .....
- $\text{XeF}_6$  cannot be stored in ..... vessel NaOH cannot be stored in ..... vessel and HF cannot be stored in .....
- Xenon fluorides are strong .....
- $\text{XeF}_4$  disproportionates to Xe(0) and Xe(VI) compounds through ..... and .....
- In 1904 Nobel prize in physics was awarded to ..... for .....
- In 1904, Nobel Prize in Chemistry was awarded to ..... for .....
- Radon is formed by .....
- Structure of  $\text{XeF}_6$  is ..... with ..... hybridisation of Xe.
- $\text{XeF}_2$  is ..... with ..... lone pairs of electrons on ..... position.
- Bond-order of  $\text{He}_2^+$  is ..... but it is ..... due to .....

## Matrix-Match Type Questions

### I. Only One Correct

1. Match the compounds (in List I) with the structures (in List II).

| List I            | List II                 |
|-------------------|-------------------------|
| A. $\text{XeF}_4$ | 1. Distorted octahedral |
| B. $\text{XeF}_6$ | 2. Tetrahedral          |
| C. $\text{XeO}_3$ | 3. Square planar        |
| D. $\text{XeO}_4$ | 4. Pyramidal            |

2. Match the types of glass (in List I) with their characteristics (in List II).

| List I                           | List II                         |
|----------------------------------|---------------------------------|
| A. Alumino-silicate glass        | 1. Very high transparency       |
| B. Calcium-alkali silicate glass | 2. Cheap laboratory glass-ware  |
| C. Lead glass                    | 3. Optical glass                |
| D. Soda glass                    | 4. Domestic glass for window    |
|                                  | 5. Low coefficient of expansion |

3. Match molecules/ions (in List I) with their shapes (in List II).

| List I                | List II          |
|-----------------------|------------------|
| A. $\text{ClF}_3$     | 1. Square planar |
| B. $[\text{PCl}_4]^+$ | 2. T-shaped      |
| C. $\text{XeF}_4$     | 3. Tetrahedral   |
| D. $\text{XeO}_3$     | 4. Pyramidal     |

4. Match the compounds (in List I) with the structures (in List II).

| List I             | List II               |
|--------------------|-----------------------|
| A. $\text{P}_4$    | 1. Crown              |
| B. $\text{S}_8$    | 2. Dimer              |
| C. $\text{AlCl}_3$ | 3. Tetrahedral        |
| D. $\text{PCl}_5$  | 4. Linear             |
|                    | 5. Trigonal bipyramid |

5. Match the name of the compound (in List I) with its formula (in List II).

| List I         | List II                                                         |
|----------------|-----------------------------------------------------------------|
| A. Borax       | 1. $\text{PH}_3$                                                |
| B. Carborundum | 2. $\text{COCl}_2$                                              |
| C. Borazine    | 3. $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ |
| D. Water glass | 4. $\text{SiC}$                                                 |
| E. Phosgene    | 5. $\text{B}_3\text{N}_3\text{H}_6$                             |
|                | 6. $\text{Na}_2\text{SiO}_3$                                    |

6. Match the acids (in List I) with number of acid salts formed by them (in List II).

| List I                  | List II |
|-------------------------|---------|
| A. Hypophosphorus acid  | 1. Two  |
| B. Orthophosphorus acid | 2. Zero |
| C. Orthophosphoric acid | 3. One  |
| D. Melliic acid         | 4. Five |

7. Match the reactions of metals with dilute  $\text{HNO}_3$  (in List I) with the nitrogen compounds (obtained by oxidation/reduction (in List II).

| List I                             | List II                     |
|------------------------------------|-----------------------------|
| A. $\text{Mg} + \text{dil. HNO}_3$ | 1. NO                       |
| B. $\text{Zn} + \text{dil. HNO}_3$ | 2. $\text{H}_2$             |
| C. $\text{Sn} + \text{dil. HNO}_3$ | 3. $\text{N}_2\text{O}$     |
| D. $\text{Pb} + \text{dil. HNO}_3$ | 4. $\text{NH}_4\text{NO}_3$ |

## II. One or More Correct

1. Match manufacturing process (in Column I) with catalyst used (in Column II).

| Column I                                                                 | Column II            |
|--------------------------------------------------------------------------|----------------------|
| A. $\text{Bi}^{3+} \longrightarrow (\text{BiO})^+$                       | 1. Heat              |
| B. $[\text{AlO}_2]^- \longrightarrow \text{Al}(\text{OH})_3$             | 2. Hydrolysis        |
| C. $\text{SiO}_4^{4-} \longrightarrow \text{Si}_2\text{O}_7^{6-}$        | 3. Acidification     |
| D. $(\text{B}_4\text{O}_7^{2-}) \longrightarrow [\text{B}(\text{OH})_3]$ | 4. Dilution by water |

- 2. Match the species in Column I with their corresponding properties in Column II.**

| Column I                    | Column II                               |
|-----------------------------|-----------------------------------------|
| A. $\text{XeO}_3$           | 1. Hydrolysis product of $\text{XeF}_6$ |
| B. $\text{XeOF}_4$          | 2. $sp^3$                               |
| C. $\text{XeO}_2\text{F}_4$ | 3. $sp^3d^2$                            |
| D. $\text{XeO}_3\text{F}_2$ | 4. Tetrahedral                          |
| E. $\text{XeO}_4$           | 5. Trigonal pyramidal                   |
|                             | 6. Square pyramidal                     |
|                             | 7. Trigonal bipyramidal                 |

## Integer Answer Types

**This section contains 8 questions.**

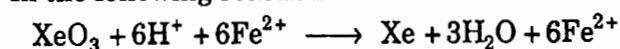
The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respectively question numbers in the *ORS* have to be darkened. For example, if the correct answers to question number *X, Y, Z* and *W* (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will like the following

| X | Y | Z | W |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 1 | 1 | 1 | 1 |
| 2 | 2 | 2 | 2 |
| 3 | 3 | 3 | 3 |
| 4 | 4 | 4 | 4 |
| 5 | 5 | 5 | 5 |
| 6 | 6 | 6 | 6 |
| 7 | 7 | 7 | 7 |
| 8 | 8 | 8 | 8 |
| 9 | 9 | 9 | 9 |

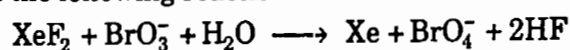
## Set I

1. In  $\text{XeF}_4$  there are ..... lone pairs of electron.
2. There are total of .....  $\pi$ -bonds in  $\text{XeO}_3$ .
3.  $s$ -character in  $\text{XeO}_4$  is  $1/\text{.....}$  of total hybrid orbitals.
4.  $\text{XeF}_4$  disproportionates in aqueous solution to  $\text{Xe}(0)$  and  $\text{Xe(VI)}$ .  $\text{Xe(VI)}$  is formed from which oxidation state (.....)
5. For inert gases  $\frac{C_p}{C_v} = \frac{5}{\dots}$
6. Bond-order of  $\text{He}_2^{2+}$  is .....

7. In the following reaction

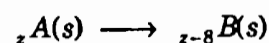

$$\text{equivalent mass of XeO}_3 = \frac{\text{molar mass}}{\dots\dots\dots}$$

8. In the following reaction


$$\text{equivalent mass of BrO}_3^- = \frac{\text{molar mass}}{\dots\dots\dots}$$

## Set II

1. Electrons left in the valence shell when Xe is converted to  $\text{XeF}_6$  is .....
2. Total number of hybrid orbitals in  $\text{XeO}_3$  is .....
3.  $A(s)$  changes to  $B(s)$  in a nuclear reaction by

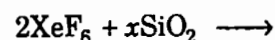


emission of  $\alpha$ -particles only. Pressure exerted per unit volume in a closed vessel at temperature  $T$  K after two half-life was  $x RT$ . What is value of  $x$ ?

4. Number phases in the following equilibrium is



5.  $\text{XeF}_6$  reacts with quartz forming  $\text{XeO}_3$



What is value of  $x$ ?

6. Out of F, Cl, Br, I, Xe, He, Ne, O, how many forms compounds with positive oxidation state?
7. 500 mL of chlorine contaminated water is treated with KI and mixture required 100 mL of 0.01 M hypo. What is concentration of  $\text{Cl}_2$  in millimoles per litre?
8. Out of the following how many have Xe in  $sp^3d$  hybridisation?  $\text{XeF}_2$ ,  $\text{XeF}_4$ ,  $\text{XeF}_6$ ,  $\text{XeOF}_2$ ,  $\text{XeO}_3$ ?

## Test Yourself on the Periodic Table

- 1. Locate each of the following elements on the Periodic Table:**

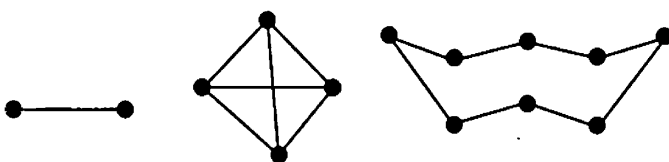
A grid of 100 squares arranged in a 10x10 pattern. The top row is missing the first square, and the bottom row is missing the last square. This grid is used for the '100 Squares' activity.

- Element with the lowest ionisation energy.
- Most electronegative element.
- Group 14 (IVA) element with the largest atomic radius.
- Group 16 (VIA) element with the smallest atomic radius.
- Group 13 (IIIA) element that is a semiconductor.
- Group 15 (VA) element that forms the strongest  $\pi$ -bonds.

2. Locate the following element on the Periodic Table

- Element that are gases at room temperature.
- A non-metal that is a liquid at 25°C.
- Non-metals that are solids at 25°C.
- Elements that exist as diatomic molecules at 25°C.

3. Consider the six, second and third-row elements in group 15–17 of the Periodic Table. Possible molecular structures for common allotropes of these elements are shown below:



I                      II                      III

- What is the molecular structure of each of the six elements?
- Using electron-dot structure explain why each element has its particular molecular structure?
- Explain why nitrogen and phosphorus have different molecular structures, and why?
- Oxygen and sulphur have different molecular structures but fluorine and chlorine have the same molecular structure.

4. Locate the following elements on the Periodic Table

- Element *X* that form compound *XN* with nitrogen.

- Element with maximum electron-affinity.
- Element of group 14 (IVA) that form mixed oxide.
- Elements which together form artificial diamond.

5. Out of the elements *A*, *B*, *C*, *D*, *E*, *F* which element

- is used for glass-cutter?
- shows inert-pair effect?
- whose carbide on reaction with  $\text{H}_2\text{O}$  forms  $\text{CH}_4$ ?
- whose diatomic gas is used as inert medium?
- whose silver salt is used in artificial rain?
- whose tetrafluoride uses  $sp^3d^2$ -hybrid orbitals?

6. Out of the elements marked as *a*, *b*, *c*, *d* and *e*

- Which element is a part of borax?
- Which element (in diatomic state) is liquid at room temperature?
- Which element is used in match-boxes?
- Which element along with Cu used in red traffic-light?
- Which element is radioactive?

7. Consider the Periodic Table and locate the

- elements with  $ns^2np^1$  valence-shell electron configuration.
- element which has been recently (Aug, 2003) named as Ds by IUPAC
- elements which form positive and negative oxidation state in *p*-block.

# Answers & Solutions

## Master Exercises

### Exercise 1

#### Short Answer Type Questions

1. Chemical inertness of lighter noble gases, *i.e.*, He, Ne and Ar, and rare abundance of comparatively reactive noble gases, *i.e.*, Kr, Xe and Rn were the reasons for the late discovery of noble gases.
2. Lord Rayleigh found that the density of nitrogen isolated from air was consistently about 0.5% higher than that of the nitrogen obtained chemically from ammonia. This observation made Lord Rayleigh suspect that there may be an additional gaseous element in air.
3. Boiling point is directly proportional to the van der Waals' forces between the atoms/molecules. More is the force of attraction, higher is the temperature required to overcome these binding force and higher will be the boiling point.
4. As we move down the group from He to Rn, the van der Waals' force of attraction between the noble gas atoms increases giving rise to a steady increase in boiling points.
5. Valence shells of He and Ne are completely filled, so they have no tendency to lose, gain or share electrons. Because of these reasons, compounds of He and Ne are not known.

6. Because the noble gases have extremely low reactivity, they need the strongest oxidising agents to form compounds.
7. In clathrates, the noble gases are held by weak van der Waals' forces which increase with the increase in the polarisability of the noble gas down the group. Therefore, the tendency to form clathrates increases down the group.
8. Terrestrial helium originated from the decay of radioactive elements in rocks.

#### Analytical Questions

1. The very fact that the first ionisation energy of xenon is slightly less than that of oxygen, led Bartlett to think that like oxygen, xenon can also be oxidised by  $\text{PtF}_6$ .
2. Oxygen and xenon which have ionisation energies,  $1180 \text{ kJ mol}^{-1}$  and  $1170 \text{ kJ mol}^{-1}$ , respectively, can be oxidised by  $\text{PtF}_6$  while nitrogen having comparatively much higher ionisation energy,  $1403 \text{ kJ mol}^{-1}$  cannot be oxidised, so a compound of the type  $[\text{N}_2]^+[\text{PtF}_6]^-$  cannot be formed.
3. On the basis of comparatively high polarisability and low ionisation energy, radon is expected to form more stable compounds. But because of very short half-life, its compounds are highly unstable.

### Exercise 2

#### Only One Option Correct

- |         |         |         |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b)  | 2. (a)  | 3. (c)  | 4. (c)  | 5. (c)  | 6. (d)  | 7. (a)  | 8. (b)  | 9. (d)  | 10. (c) |
| 11. (a) | 12. (a) | 13. (a) | 14. (b) | 15. (b) | 16. (a) | 17. (d) | 18. (a) | 19. (d) | 20. (c) |
| 21. (a) | 22. (d) | 23. (a) | 24. (d) | 25. (c) | 26. (d) | 27. (b) | 28. (a) | 29. (c) | 30. (d) |

#### One or More Than One Options Correct

1. (a,b,c,d)
2. (c)
3. (a,b)
4. (a,b,d)
5. (c)
6. (a,c)
7. (a,b,c,d)
8. (c)
9. (a,b,c,d)
10. (b)

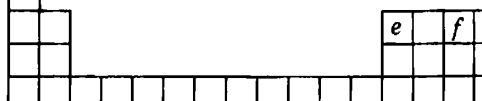
#### Passage Comprehension Questions

##### Passage 1

1. (a)
2. (a)

##### Passage 2

1. (a)
2. (c)
3. (a)

1. 

2.

(a)

(b)

(c)

(d)

3. (a) I :  $N_2$ ,  $O_2$ ,  $F_2$ ,  $Cl_2$ ; II :  $P_4$ ; III :  $S_8$  (b) Refer text

(c) Refer text (d) Refer text

(a) Al, XN is AlN (b) Cl

(c)  $Pb_3O_4$  : a mixed oxide  $2PbO \cdot PbO_2$ 

(d) SiC is artificial diamond.

4.

5. (a) B (b) C (c) A (d) D (e) F (f) E.

6. (i) a, (ii) d, (iii) b, (iv) c, (v) e.

7.

(a)

(b) Ds

(c)



# Appendices

## Appendix I. Important Processes

|                                             |                                               |
|---------------------------------------------|-----------------------------------------------|
| Bosch process                               | Hydrogen                                      |
| Castner process                             | Sodium                                        |
| Down process                                | Sodium                                        |
| Nelson cell                                 | NaOH                                          |
| Castner-Kellner cell                        | NaOH                                          |
| Pidgeon process                             | Mg                                            |
| Lowig process                               | NaOH                                          |
| Solvay process or Ammonia soda process      | $\text{Na}_2\text{CO}_3$ and $\text{NaHCO}_3$ |
| Leblanc process                             | $\text{K}_2\text{CO}_3$ , NaOH                |
| Precht process                              | $\text{K}_2\text{CO}_3$                       |
| MacArthur Forrest process (Cyanide process) | Ag                                            |
| Parke's process                             | Ag                                            |
| Pattinson's process                         | Ag                                            |
| Cupellation process                         | Ag (Purification)                             |
| Mond process                                | Ni                                            |
| Baeyer's process                            | Al                                            |
| Serpeck's process                           | Al                                            |
| Hoop's process                              | Al (Purification)                             |
| Hall heroult process                        | Al                                            |
| Goldschmidt process                         | Thermite welding                              |
| Carter process                              | Basic lead carbonate (White lead)             |
| Haber's process                             | $\text{NH}_3$                                 |
| Birkeland-Eyde process                      | NO, $\text{HNO}_3$                            |
| Ostwald process                             | NO, $\text{HNO}_3$                            |
| Deacon's process                            | $\text{Cl}_2$                                 |
| Lead chamber process                        | $\text{H}_2\text{SO}_4$                       |
| Contact process                             | $\text{H}_2\text{SO}_4$                       |
| Kaldo and L.D. process                      | Steel                                         |
| Corey-House                                 | alkane                                        |
| Oxo process                                 | alcohol                                       |
| Dow's sea water process                     | Mg                                            |
| Cyanamide process                           | $\text{NH}_3$                                 |
| Bessemer-Thomas process                     | Steel                                         |
| Siemens process                             | Steel                                         |
| Frasch process                              | Sulphur                                       |
| IMI process                                 | Ti                                            |
| Wet process                                 | $\text{H}_3\text{PO}_4$                       |
| Furnace process                             | $\text{H}_3\text{PO}_4$                       |
| Salt cake method                            | $\text{Cl}_2$                                 |
| Hargreaves process                          | $\text{Cl}_2$                                 |

## Appendix II. Some Important Compounds/ Minerals

|                                  |                                                                         |
|----------------------------------|-------------------------------------------------------------------------|
| Magnesite                        | $\text{MgCO}_3$                                                         |
| Dolomite                         | $\text{MgCO}_3 \cdot \text{CaCO}_3$                                     |
| Kieserite                        | $\text{MgSO}_4 \cdot \text{H}_2\text{O}$                                |
| Epsomite                         | $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$                               |
| Talc                             | $\text{Mg}_2(\text{Si}_2\text{O}_5)_2\text{Mg}(\text{OH})_2$            |
| Magnesia alba                    | $(\text{MgCO}_3)_x[\text{Mg}(\text{OH})_2]_y \cdot z\text{H}_2\text{O}$ |
| Sorel's cement (magnesia cement) | $\text{MgCl}_2 \cdot 5\text{MgO} \cdot x\text{H}_2\text{O}$             |
| Lime stone, marble or chalk      | $\text{CaCO}_3$                                                         |
| Gypsum                           | $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$                               |
| Plaster of Paris                 | $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$                    |
| Anhydrite                        | $\text{CaSO}_4$                                                         |
| Dolomite                         | $\text{CaCO}_3 \cdot \text{MgCO}_3$                                     |
| Fluorspar                        | $\text{CaF}_2$                                                          |
| Phosphorite                      | $\text{Ca}_3(\text{PO}_4)_2$                                            |
| Quick lime                       | $\text{CaO}$                                                            |
| Slaked lime                      | $\text{Ca}(\text{OH})_2$                                                |
| Soda lime                        | $\text{Ca}(\text{OH})_2 + \text{NaOH}$                                  |
| Chlorapatite                     | $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2$                       |
| Apatite (Fluorapatite)           | $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$                        |
| Pearl ash, Potash                | $\text{K}_2\text{CO}_3$                                                 |
| Sylvite                          | KCl                                                                     |
| Carnallite                       | $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$              |
| Felspar                          | $\text{KAlSi}_3\text{O}_8$                                              |
| Salt petre (Indian salt petre)   | $\text{KNO}_3$                                                          |
| Kainite                          | $\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$              |
| Schonite                         | $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$   |
| Permutit (Zeolite)               | $\text{Na}_2\text{Al}_2\text{SiO}_8 \cdot x\text{H}_2\text{O}$          |
| Calgon (Graham's salt)           | $(\text{NaPO}_3)_n, \text{Na}_2[\text{NH}_4(\text{PO}_3)_6]$            |
| Chile salt petre                 | $\text{NaNO}_3$                                                         |
| Salt cake                        | $\text{Na}_2\text{SO}_4$ (anhydrous)                                    |
| Glauber's salt                   | $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$                     |
| Nitre salt                       | $\text{NaHSO}_4$                                                        |
| Borax                            | $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$            |
| Soda ash (Crystal carbonate)     | $\text{Na}_2\text{CO}_3$ (anhydrous)                                    |
| Washing soda                     | $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$                     |
| Crystal carbonate                | $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$                       |
| Baking soda                      | $\text{NaHCO}_3$                                                        |

|                             |                                                                                                 |                            |                                                                   |
|-----------------------------|-------------------------------------------------------------------------------------------------|----------------------------|-------------------------------------------------------------------|
| Coinage metals              | Cu, Ag and Au                                                                                   | Aqua-regia                 | Conc. $\text{HNO}_3$ + Conc. $\text{HCl}$<br>(1 : 3 part)         |
| Caro's acid                 | $\text{H}_2\text{SO}_5$                                                                         | Anhdron                    | $\text{Mg}(\text{ClO}_4)_2$                                       |
| Marshall's acid             | $\text{H}_2\text{S}_2\text{O}_8$                                                                | Barytes or barite          | $\text{BaSO}_4$                                                   |
| Borazine                    | $\text{B}_3\text{N}_3\text{H}_6$                                                                | Baryta water               | $\text{Ba}(\text{OH})_2$ solution                                 |
| (Inorganic benzene)         |                                                                                                 | Bleaching powder           | $\text{CaOCl}_2$                                                  |
| Boron nitride               | $(\text{BN})_x$                                                                                 | Boranes                    | Hydride of boron                                                  |
| (Inorganic graphite)        |                                                                                                 | Brine                      | $\text{NaCl}$ solution                                            |
| Sylvinite                   | $(\text{NaCl} + \text{KCl})$                                                                    | Baryta                     | $\text{BaO}$                                                      |
| Bordeaux mixture            | $\text{CuSO}_4/\text{Ca}(\text{OH})_2$                                                          | Asbestos (Chrysotile)      | $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$                   |
| (fungicides)                |                                                                                                 | Spinel                     | $\text{MgAl}_2\text{O}_4$                                         |
| Copper pyrites              | $\text{CuFeS}_2$ or $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$                           | Carborundum                | $\text{SiC}$                                                      |
| Cuprite (Ruby copper)       | $\text{Cu}_2\text{O}$                                                                           | Cementite                  | $\text{FeC}$                                                      |
| Copper glance               | $\text{Cu}_2\text{S}$                                                                           | Chinese white              | $\text{ZnO}$                                                      |
| Malachite                   | $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$                                                    | Caliche                    | $\text{NaNO}_3 + \text{NaIO}_3$                                   |
| Azurite                     | $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$                                                   | Caustic potash             | $\text{KOH}$                                                      |
| Blue vitriol                | $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$                                                       | Calomel                    | $\text{Hg}_2\text{Cl}_2$                                          |
| Argentite (Silver glance)   | $\text{Ag}_2\text{S}$                                                                           | Corrosive sublimate        | $\text{HgCl}_2$                                                   |
| Horn silver (Chlorargyrite) | $\text{AgCl}$                                                                                   | Dry ice (Drikold)          | solid $\text{CO}_2$                                               |
| Ruby silver (Pyrargyrite)   | $\text{Ag}_3\text{SbS}_3$                                                                       | Freon                      | $\text{CF}_2\text{Cl}_2$                                          |
| Argentiferous galena        | $\text{PbS} + \text{Ag}_2\text{S}$                                                              | Hydrolith                  | $\text{CaH}_2$                                                    |
| Lunar caustic               | $\text{AgNO}_3$                                                                                 | Hypo                       | $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$       |
| Zinc blende                 | $\text{ZnS}$                                                                                    | Lead pencil                | Graphite                                                          |
| Calamine                    | $\text{ZnCO}_3$                                                                                 | Laughing gas               | $\text{N}_2\text{O}$                                              |
| Zincite (Red $\text{ZnO}$ ) | $\text{ZnO}$                                                                                    | Litharge (Masscote)        | $\text{PbO}$                                                      |
| Philosopher's wool          | $\text{ZnO}$                                                                                    | Lanakite                   | $\text{PbO} \cdot \text{PbSO}_4$                                  |
| Willemite                   | $\text{Zn}_2\text{SiO}_4$                                                                       | Mortar                     | Slaked lime + sand (1 : 3 in<br>water)                            |
| Bauxite                     | $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$                                               | Matte                      | $\text{Cu}_2\text{S} + \text{FeS}$                                |
| Corundum (emerald)          | $\text{Al}_2\text{O}_3$                                                                         | Minium                     | $\text{Pb}_3\text{O}_4$                                           |
| Diaspore                    | $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$                                                | Micro cosmic salt          | $\text{NaNH}_4 \cdot \text{HPO}_4$                                |
| Cryolite                    | $\text{Na}_3\text{AlF}_6$                                                                       | Milk of magnesia (Antacid) | Paste of $\text{Mg}(\text{OH})_2$ in water                        |
| Kaolinite                   | $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$                           | Marsh gas                  | $\text{CH}_4$                                                     |
| Mica                        | $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ | Nitro chalk                | $[\text{NH}_4\text{NO}_3 + (\text{NH}_4)_2\text{CO}_3]$           |
| Alum shale                  | $\text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 + \text{FeS}_2$                                      | Nitrolim                   | $\text{CaCN}_2$ (a fertilizer) + C                                |
| Alum stone (Alunite)        | $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 4\text{Al}(\text{OH})_3$          | Nitrophos                  | $\text{Ca}(\text{H}_2\text{PO}_4)_2 + 2\text{Ca}(\text{NO}_3)_2$  |
| Cassiterite (Tin stone)     | $\text{SnO}_2$                                                                                  | Baking powder              | $\text{NaHCO}_3 + \text{Ca}(\text{H}_2\text{PO}_4)_2$<br>+ Starch |
| Galena                      | $\text{PbS}$                                                                                    | Oil of vitriol             | Conc. $\text{H}_2\text{SO}_4$                                     |
| Anglesite                   | $\text{PbSO}_4$                                                                                 | Oleum                      | $\text{H}_2\text{S}_2\text{O}_7$                                  |
| Cerussite                   | $\text{PbCO}_3$                                                                                 | Phosgene                   | $\text{COCl}_2$                                                   |
| Lanakite                    | $\text{PbO} \cdot \text{PbSO}_4$                                                                | Pig iron                   | Impure form of iron                                               |
| Masscote (Litharge)         | $\text{PbO}$                                                                                    | Producer gas               | A mixture of $\text{CO} + \text{N}_2 + \text{H}_2$                |
| Haematite (Red haematite)   | $\text{Fe}_2\text{O}_3$                                                                         | Quartz (agate)             | $\text{SiO}_2$                                                    |
| Limonite                    | $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$                                               | Quick silver               | Hg                                                                |
| (Brown haematite)           |                                                                                                 | Refrigerant                | $\text{CO}_2, \text{NH}_3, \text{CF}_2\text{Cl}_2$ etc.           |
| Magnetite                   | $\text{Fe}_3\text{O}_4$                                                                         | Red lead                   | $\text{Pb}_3\text{O}_4$                                           |
| Siderite (Spathic iron ore) | $\text{FeCO}_3$                                                                                 | Rochelle salt              | Sodium-potassium tartrate                                         |
| Iron pyrites                | $\text{FeS}_2$                                                                                  | Rust                       | $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$                 |
| Mohr's salt                 | $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$                      |                            |                                                                   |
| Green vitriol (copperas)    | $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$                                                       |                            |                                                                   |
| Asbestos                    | $\text{CaMg}_3(\text{SiO}_3)_4$                                                                 |                            |                                                                   |

|                                             |                                                                |                               |                                                                                                                                                                                                                                 |
|---------------------------------------------|----------------------------------------------------------------|-------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| TNT                                         | Trinitro toluene (an explosive)                                | Natural explosive             | $\text{NCl}_3$                                                                                                                                                                                                                  |
| TNB                                         | Trinitro benzene (an explosive)                                | Some polymorphic elements     | O, S, P                                                                                                                                                                                                                         |
| Tincal                                      | $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$   | Wrought iron                  | Pure form of iron                                                                                                                                                                                                               |
| Water glass                                 | $\text{Na}_2\text{SiO}_3$                                      | Zinc white                    | $\text{ZnO}$                                                                                                                                                                                                                    |
| Water gas                                   | $\text{CO} + \text{H}_2$                                       | Olivine                       | $(\text{Mg}, \text{Fe})_2\text{SiO}_4$                                                                                                                                                                                          |
| Yperite                                     | Mustard gas                                                    | Strontianite                  | $\text{SrCO}_3$                                                                                                                                                                                                                 |
| Langbeinite                                 | $\text{K}_2\text{Mg}(\text{SO}_4)_3$                           | Tincture iodine (antiseptic)  | $\text{I}_2$ in alcohol                                                                                                                                                                                                         |
| Celestite                                   | $\text{SrSO}_4$                                                | Some commonly used reductants | $\text{SO}_2, \text{H}_2\text{S}, \text{Cl}_2$                                                                                                                                                                                  |
| Artificial explosive                        | Dynamite                                                       | Dry bleacher                  | Bleaching powder                                                                                                                                                                                                                |
| First Noble Prize of chemistry was given to | vant Hoff                                                      | Amphoteric oxides             | $\text{O}_3$                                                                                                                                                                                                                    |
| Some commonly used bleaching substances     | $\text{H}_2\text{O}_2, \text{SO}_2, \text{SO}_3, \text{Cl}_2$  | Some isomorphous substances   | $\text{ZnO}, \text{PbO}, \text{Al}_2\text{O}_3, \text{SnO}, \text{BeO}$                                                                                                                                                         |
| Neutral oxides of non-metals                | $\text{CO}, \text{N}_2\text{O}, \text{NO}, \text{H}_2\text{O}$ |                               | $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{MgSO}_4 \cdot 7\text{H}_2\text{O}, \text{ZnSO}_4 \cdot 7\text{H}_2\text{O}, \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}, \text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ |

### Appendix III. Important Reagents

| Reagents                     | Constituents                                                                        | Uses                                                          |
|------------------------------|-------------------------------------------------------------------------------------|---------------------------------------------------------------|
| Aqua regia,                  | Conc. $\text{HCl}$ and conc. $\text{HNO}_3$ (1 : 3 by volume)                       | To dissolve noble metals Au, Pt                               |
| Baeyer's reagent             | Cold alkaline $\text{KMnO}_4$                                                       | To test unsaturation (alkene, alkyne) in organic compounds    |
| Baryta water                 | 5% $\text{Ba}(\text{OH})_2$ solution                                                | As a medicine to control digestive system                     |
| Barfoed reagent              | $(\text{CH}_3\text{COO})_2\text{Cu}$ and $\text{CH}_3\text{COOH}$                   | To make distinction between monosaccharides and disaccharides |
| Brown's catalyst             | Nickel boride                                                                       | To prepare stereoisomer from alkene by hydrogenation          |
| Ceric ammonium nitrate (CAN) | CAN in $\text{HNO}_3$                                                               | To test alcohols                                              |
| Candy water                  | $\text{KMnO}_4$ solution                                                            | For oxidation                                                 |
| Denige's reagent             | Acidic solution of $\text{HgO}$                                                     | To test citrate                                               |
| Etard's reagent              | $\text{CrO}_2\text{Cl}_2$                                                           | Oxidising agent                                               |
| Fehling's solution           | A : $\text{CuSO}_4$ solution<br>B : Sodium potassium tartrate                       | To test $-\text{CHO}$ (only aliphatic) and reducing sugars    |
| Fenton's reagent             | $\text{FeSO}_4$ (or other $\text{Fe}^{2+}$ ion) and $\text{H}_2\text{O}_2$          | To oxidise polyhydric alcohols                                |
| Fusion mixture               | $\text{Na}_2\text{CO}_3$ and $\text{K}_2\text{CO}_3$                                | In salt mixture analysis                                      |
| Grignard's reagent           | $\text{RMgX}$ ( $R$ = alkyl, aryl $X = \text{Cl}, \text{Br}, \text{I}$ )            | To synthesise alcohols, aldehydes, ketones acids, etc.        |
| Hinsberg's reagent           | Benzene sulphonyl chloride, ( $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ )          | To separate and to distinguish 1°, 2° and 3° amines           |
| Lucas reagent                | Conc. $\text{HCl}$ and anhydrous $\text{ZnCl}_2$                                    | To distinguish 1°, 2° and 3° alcohols                         |
| Millon's reagent             | $\text{Hg}(\text{NO}_3)_2, \text{Hg}_2(\text{NO}_3)_2$ in $\text{HNO}_3$            | To test proteins                                              |
| Magnesia mixture             | $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}, \text{NH}_4\text{Cl}$ , and $\text{NH}_3$ | To test arsenate and phosphate                                |
| Molisch's reagent            | Alcoholic solution of $\alpha$ -naphthol                                            | To test carbohydrates                                         |
| Nessler's reagent            | $\text{K}_2\text{HgI}_4$ in $\text{NaOH}$                                           | To test $\text{NH}_4^+$                                       |
| Schiff's reagent             | $p$ -rosaniline hydrochloride solution decolourised by $\text{SO}_2$                | To test $-\text{CHO}$ group                                   |
| Sodium nitroprusside         | $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$                                      | To test $\text{S}^{2-}$ ion (sulphide)                        |
| Tollen's reagent             | Ammoniacal $\text{AgNO}_3$                                                          | To test $-\text{CHO}$ group and reducing sugars               |

## Appendix IV. Scientists and Their Contributions

| Scientist           | Contribution                                                                |
|---------------------|-----------------------------------------------------------------------------|
| Anderson            | Discovery of positron                                                       |
| Aspidin, J          | Portland cement                                                             |
| Aston, F. William   | Isolation of non-radioactive elements and discovery of mass-spectrograph    |
| Bacon, R            | Gun powder                                                                  |
| Bohr                | Atomic model, Long form of Periodic Table                                   |
| Becquerrel H.       | Radioactivity                                                               |
| Berzelius, J.J.,    | Modern system of symbolising elements, relative atomic masses.              |
| Bunsen R            | Bunsen burner                                                               |
| Chadwick            | Discovery of neutron                                                        |
| Curie I.J.          | Radioactive elements                                                        |
| Fermi E.            | Nuclear reactor                                                             |
| Goldstein           | Discovery of proton                                                         |
| Mendeleef           | Periodic Table                                                              |
| Meyer L.            | Classification of elements based upon atomic volume                         |
| Moseley             | Modern Periodic Law                                                         |
| Pauling Linus C.    | Pauling scale of electronegativity                                          |
| Ramsay, Sir William | Discovery of noble gases Ar, Ne, He                                         |
| Rontgen             | Discovery of X-ray                                                          |
| Seaborg G.T.        | Discovery of <i>trans</i> -uranium elements                                 |
| Solvay, E           | Solvay ammonia soda process for the manufacture of $\text{Na}_2\text{CO}_3$ |
| Teller E            | Hydrogen bomb                                                               |
| Thomson J.J.        | Discovery of electron, $e/m$ ratio of electron, photoelectric effect        |
| Yukawa              | Discovery of Mesons                                                         |
| Wohler F.           | Synthesis of first organic compound (urea) from inorganic salt              |

## Appendix V. Facts to Remember

|                                                        |                      |
|--------------------------------------------------------|----------------------|
| Most reactive solid element                            | : Li                 |
| Most reactive liquid element                           | : Cs                 |
| Most reactive gaseous element                          | : F                  |
| Highest electronegativity                              | : F                  |
| Highest ionisation potential                           | : He                 |
| Lowest ionisation potential                            | : Cs                 |
| Lowest electron affinity                               | : Noble gases (zero) |
| Highest electron affinity                              | : Cl                 |
| Liquid element of radioactive nature                   | : Francium (Fr)      |
| Total number of radioactive elements in Periodic Table | : 25                 |

|                                               |                            |
|-----------------------------------------------|----------------------------|
| Volatile <i>d</i> -block elements             | : Zn, Cd, Hg               |
| Element containing no neutron                 | : $^1_1\text{H}$           |
| Most abundant element of earth                | : Oxygen (O)               |
| Rarest element of earth                       | : Astatine (At)            |
| Most abundant metal of earth                  | : Al                       |
| Element having maximum tendency for catention | : Carbon                   |
| Lightest element                              | : H                        |
| Heaviest naturally occurring element          | : $^{238}\text{U}$         |
| Poorest conductor of current                  | : Pb(metal), S(non-metal)  |
| Amphoteric non-metal                          | : Si                       |
| Elements showing diagonal relationship        | : Li—Mg; Be—Al; B—Si       |
| Metalloids elements                           | : B, Si, Ge, As, Sb, Te    |
| Non-metals having metallic lustre             | : Iodine, graphite         |
| Element sublime on heating                    | : I                        |
| Noble metals                                  | : Au, Pt                   |
| Amphoteric metals                             | : Zn, Al, Sn, Pb           |
| Non-metal having highest m.p., b.p.           | : Diamond                  |
| Metals showing highest oxidation number.      | : Ru, Os                   |
| Element having highest tensile strength       | : Boron                    |
| Coolant in nuclear reactors                   | : $\text{D}_2\text{O}$     |
| Best electricity conductor among metals       | : Ag                       |
| Best conductor among non-metals               | : Graphite                 |
| Most poisonous element                        | : Pu                       |
| Liquid non-metal                              | : $\text{Br}_2$            |
| Liquid metals                                 | : Hg, Ga, Cs, Fr, Eka      |
| Element kept in water                         | : P                        |
| Elements kept in kerosene oil                 | : Na, K, $\text{I}_2$ , Cs |
| Dry ice                                       | : $\text{CO}_2$            |
| Most recently elements named by IUPAC         | : Ds (atomic number = 110) |
| 'All purpose' grease                          | : Lithium stearate         |
| Old name of Astatine                          | : Albamine                 |
| Most abundant gas in atmosphere               | : $\text{N}_2$             |
| Rarest gas in atmosphere                      | : Rn                       |
| Lightest gas in atmosphere                    | : $\text{H}_2$             |
| Metal with highest m.p.                       | : W                        |
| Metal with lowest m.p.                        | : Hg                       |
| Non-metal with highest refractive index       | : Diamond                  |

|                                                     |                                                                                       |
|-----------------------------------------------------|---------------------------------------------------------------------------------------|
| Lowest refractive index                             | : Air                                                                                 |
| Lowest b.p.                                         | : H <sub>2</sub>                                                                      |
| Group containing highest number of gaseous elements | : Group 18 (Noble gases)                                                              |
| Most electrovalent compound                         | : CsF                                                                                 |
| Heaviest solid metal                                | : Os                                                                                  |
| Lightest solid metal                                | : Li                                                                                  |
| Lightest solid non-metal                            | : B                                                                                   |
| Hardest naturally occurring non-metal               | : Diamond                                                                             |
| Hardest artificial substance good conductor of heat | : B <sub>4</sub> C (norbide)                                                          |
| but bad conductor of electricity                    | : Mica                                                                                |
| Strongest basic hydroxide                           | : CsOH                                                                                |
| Strongest basic oxide                               | : CsO <sub>2</sub> (caesium peroxide).                                                |
| Most stable metal carbonate                         | : Cs <sub>2</sub> CO <sub>3</sub>                                                     |
| Element with highest radioactivity                  | : Ra                                                                                  |
| Highest radio-isotope                               | : Tritium ( <sup>3</sup> H)                                                           |
| Compound with maximum covalent nature               | : H <sub>2</sub> , N <sub>2</sub> , O <sub>2</sub> , Cl <sub>2</sub> (diatomic gases) |
| Strongest reducing agent                            | : Azide (N <sub>3</sub> <sup>-</sup> )                                                |
| Strongest oxidising agent                           | : OF <sub>2</sub>                                                                     |
| Largest atomic size                                 | : Cs                                                                                  |
| Smallest atomic size                                | : H                                                                                   |
| Smallest anion                                      | : H <sup>-</sup> (hydrides)                                                           |
| First Noble Prize in Chemistry                      | : van't Hoff                                                                          |
| Most abundant noble gas                             | : Ar                                                                                  |
| Most abundant element in human body                 | : Oxygen                                                                              |
| Most abundant gas in Sun                            | : H <sub>2</sub>                                                                      |
| Most abundant gases in universe                     | : H <sub>2</sub> , He                                                                 |
| Element with maximum number isotopes                | : Ag (46)                                                                             |
| Element with minimum number of isotopes             | : H(3)                                                                                |
| Element with maximum number of allotropes           | : Sn                                                                                  |
| Softest form of carbon                              | : Lamp black                                                                          |
| Latest allotrope of carbon                          | : Fullerene or bucky ball                                                             |
| Strongest acid                                      | : HSO <sub>5</sub> F + 90% SbF <sub>5</sub> called magic acid                         |
| Most reactive form of P                             | : White                                                                               |
| Least reactive form of P                            | : Red                                                                                 |
| Purest form of silica                               | : Quartz                                                                              |
| Most ductile metal                                  | : Gold                                                                                |

## Appendix VI. Important Alloys

| Alloy                | Component            | Alloy                         | Component          |
|----------------------|----------------------|-------------------------------|--------------------|
| Aluminium bronze     | Cu, Al               | Electron                      | Mg, Zn             |
| Alpax                | Si, Al               | Ferrochrome                   | Fe, Cr             |
| Alnico               | Al, Ni, Co, Fe, Cu   | Ferromanganese                | Fe, Mn             |
| γ-alloy              | Al, Cu, Mg, Ni       | Ferrosilicon (silicon steel)  | Fe, Si             |
| Amalgam              | Metal coated with Hg | German silver (Nickel silver) | Cu, Zn, Ni         |
| Brass                | Cu, Zn               | Gun metal                     | Cu, Sn, Zn         |
| Bronze               | Cu, Sn               | Hydrone                       | Na, Pb             |
| Bell metal           | Cu, Sn               | Hastelloy C Nicrome           | Ni, Cr             |
| Britannia metal      | Sn, Sb, Cu, Zn       | Invar                         | Fe, Ni             |
| Babbitt metal        | Sn, Sb, Cu           | LA 141                        | Li, Al, Mg         |
| Bearing metal        | Cu, Zn, Sb           | Magnalium                     | Mg, Al             |
| Coin alloy (white)   | Cu, Ag, Zn, Ni       | Manganium                     | Ni, Cu, Mn         |
| Coin alloy (red)     | Cu, Zn, Sn           | Manganese steel               | Fe, C, Mn          |
| Constantan           | Cu, Ni               | Monel metal                   | Cu, Ni, Fe, Mn     |
| Cunico               | Cu, Ni, Fe, Co       | Nichrome                      | Ni, Cr, Fe, Mn     |
| Delta metal          | Cu, Zn, Fe           | Newton metal                  | Sn, Pb             |
| Dutch metal          | Cu, Zn               | Nickeloy                      | Ni, Cu, Al         |
| Dental alloy         | Sn, Hg, Ag           | Nickel steel                  | Ni, Fe             |
| Devarda's alloy      | Cu, Zn, Al           | Nimonic series                | Ni, Cr, Co, Al, Ti |
| Duralumin            | Al, Cu, Mg, Zn       | Perm alloy                    | Ni, Fe, C          |
| Phosphor bronze      | Cu, Sn, P            | Pewter                        | Pb, Sn             |
| Rolled gold          | Cu, Al               | Platinite                     | Fe, Ni             |
| Rose metal           | Bi, Zn, Pb, Cd       | Type metal                    | Pb, Sb, Sn         |
| Soft silver (solder) | Sn, Pb               | White metal                   | Cu, Sb, Sn         |
| Stainless steel      | Fe, Ni, Cr, C        | Wood's metal                  | Bi, Pb, Sn, Cd     |

## Appendix VII. Alloy Steels

Mechanical and other properties of steel are greatly modified by alloying with different metals and silicon. Some of these alloy steels are :

| Type                  | Composition                             | Properties                                                       | Uses                                            |
|-----------------------|-----------------------------------------|------------------------------------------------------------------|-------------------------------------------------|
| Silicon steel         | 3.5% Si and very little carbon          | magnetic                                                         | electromagnets and transformers.                |
| Stainless steel       | 12-15% Cr                               | resists corrosion and action of acids                            | Stainless steel utensils                        |
| Manganese steel       | 12-13% Mn                               | resistant to wear                                                | grinding machinery, safe, rock drill            |
| Cobalt steel          | up to 35% cobalt                        | magnetic                                                         | permanent magnets                               |
| Nickel steel          | 2-4% Ni                                 | high tensile strength                                            | cables, propeller shafts gears                  |
| Invar                 | up to 36% Ni                            | low coefficient of thermal expansion                             | scientific instruments                          |
| Chrome-nickel steel   | 1-4% Ni; 0.5-2% Cr                      | high tensile strength, great corrosion resistance                | motor car and bicycle parts                     |
| Platinite             | 46% Ni                                  | coefficient of thermal expansion same as that of glass           | glassmetal-seals, electric bulbs                |
| Chrome-vanadium steel | 1-10% Cr, 0.14-0.55% V                  | high tensile strength, resistant to stress and torsion           | automobile axles and springs                    |
| Tungsten steel        | 10-20% W, 3-8% Cr                       | hard, corrosion-resistant and retains temper at high temperature | high-speed cutting tools                        |
| Molybdenum steel      | 6-7% Mo                                 | retains temper at high temperature                               | high-speed cutting tools                        |
| Misch-metal           | 70% Ce and traces of rare-earth metals. | produces spark on strike                                         | to produce spark in gas and cigarette lighters. |

## Appendix VIII. Electronic Configurations of the Atoms of the Elements

| Element | Atomic Number | Populations of Subshells |    |    |    |    |    |    |    |    |    |    |  |   |  |
|---------|---------------|--------------------------|----|----|----|----|----|----|----|----|----|----|--|---|--|
|         |               | 1s                       | 2s | 2p | 3s | 3p | 3d | 4s | 4p | 4d | 4f | 5s |  |   |  |
| H       | 1             | 1                        |    |    |    |    |    |    |    |    |    |    |  |   |  |
| He      | 2             | 2                        |    |    |    |    |    |    |    |    |    |    |  |   |  |
| Li      | 3             | 2                        | 1  |    |    |    |    |    |    |    |    |    |  |   |  |
| Be      | 4             | 2                        | 2  |    |    |    |    |    |    |    |    |    |  |   |  |
| B       | 5             | 2                        | 2  | 1  |    |    |    |    |    |    |    |    |  |   |  |
| C       | 6             | 2                        | 2  | 2  |    |    |    |    |    |    |    |    |  |   |  |
| N       | 7             | 2                        | 2  | 3  |    |    |    |    |    |    |    |    |  |   |  |
| O       | 8             | 2                        | 2  | 4  |    |    |    |    |    |    |    |    |  |   |  |
| F       | 9             | 2                        | 2  | 5  |    |    |    |    |    |    |    |    |  |   |  |
| Ne      | 10            | 2                        | 2  | 6  |    |    |    |    |    |    |    |    |  |   |  |
| Na      | 11            | Neon core                |    |    | 1  |    |    |    |    |    |    |    |  |   |  |
| Mg      | 12            |                          |    |    | 2  |    |    |    |    |    |    |    |  |   |  |
| Al      | 13            |                          |    |    | 2  | 1  |    |    |    |    |    |    |  |   |  |
| Si      | 14            |                          |    |    | 2  | 2  |    |    |    |    |    |    |  |   |  |
| P       | 15            |                          |    |    | 2  | 3  |    |    |    |    |    |    |  |   |  |
| S       | 16            |                          |    |    | 2  | 4  |    |    |    |    |    |    |  |   |  |
| Cl      | 17            |                          |    |    | 2  | 5  |    |    |    |    |    |    |  |   |  |
| Ar      | 18            | 2                        | 2  | 6  | 2  | 6  |    |    |    |    |    |    |  |   |  |
| K       | 19            | Argon core               |    |    |    |    | 1  |    |    |    |    |    |  |   |  |
| Ca      | 20            |                          |    |    |    |    | 2  |    |    |    |    |    |  |   |  |
| Sc      | 21            |                          |    |    |    |    | 1  | 2  |    |    |    |    |  |   |  |
| Ti      | 22            |                          |    |    |    |    | 2  | 2  |    |    |    |    |  |   |  |
| V       | 23            |                          |    |    |    |    | 3  | 2  |    |    |    |    |  |   |  |
| Cr      | 24            |                          |    |    |    |    | 5  | 1  |    |    |    |    |  |   |  |
| Mn      | 25            |                          |    |    |    |    | 5  | 2  |    |    |    |    |  |   |  |
| Fe      | 26            |                          |    |    |    |    | 6  | 2  |    |    |    |    |  |   |  |
| Co      | 27            |                          |    |    |    |    | 7  | 2  |    |    |    |    |  |   |  |
| Ni      | 28            |                          |    |    |    |    | 8  | 2  |    |    |    |    |  |   |  |
| Cu      | 29            |                          |    |    |    |    | 10 | 1  |    |    |    |    |  |   |  |
| Zn      | 30            |                          |    |    |    |    | 10 | 2  |    |    |    |    |  |   |  |
| Ga      | 31            |                          |    |    |    |    | 10 | 2  |    |    |    |    |  |   |  |
| Ge      | 32            |                          |    |    |    |    | 10 | 2  | 1  |    |    |    |  |   |  |
| As      | 33            |                          |    |    |    |    | 10 | 2  | 2  |    |    |    |  |   |  |
| Se      | 34            |                          |    |    |    |    | 10 | 2  | 3  |    |    |    |  |   |  |
| Br      | 35            |                          |    |    |    |    | 10 | 2  | 4  |    |    |    |  |   |  |
| Kr      | 36            | 2                        | 2  | 6  | 2  | 6  | 10 | 2  | 6  |    |    |    |  |   |  |
| Rb      | 37            | Krypton core             |    |    |    |    |    |    |    | 1  |    |    |  |   |  |
| Sr      | 38            |                          |    |    |    |    |    |    |    | 2  |    |    |  |   |  |
| Y       | 39            |                          |    |    |    |    |    |    |    |    |    |    |  |   |  |
| Zr      | 40            |                          |    |    |    |    |    |    |    | 1  |    | 2  |  |   |  |
| Nb      | 41            |                          |    |    |    |    |    |    |    | 2  |    | 2  |  |   |  |
| Mo      | 42            |                          |    |    |    |    |    |    |    | 3  |    | 2  |  |   |  |
| Tc      | 43            |                          |    |    |    |    |    |    |    | 5  |    | 1  |  |   |  |
| Ru      | 44            |                          |    |    |    |    |    |    |    | 5  |    | 2  |  |   |  |
| Rh      | 45            |                          |    |    |    |    |    |    |    | 7  |    | 1  |  |   |  |
| Pd      | 46            |                          |    |    |    |    |    |    |    | 8  |    | 1  |  |   |  |
| Ag      | 47            |                          |    |    |    |    |    |    |    | 10 |    |    |  | 1 |  |
| Cd      | 48            |                          |    |    |    |    |    |    |    | 10 |    |    |  | 2 |  |

| Element | Atomic Number | Populations of Subshells |    |    |    |    |    |    |    |    |    |
|---------|---------------|--------------------------|----|----|----|----|----|----|----|----|----|
|         |               | 4d                       | 4f | 5s | 5p | 5d | 5f | 6s | 6p | 6d | 7s |
| In      | 49            | 10                       |    | 2  | 1  |    |    |    |    |    |    |
| Sn      | 50            | 10                       |    | 2  | 2  |    |    |    |    |    |    |
| Sb      | 51            | 10                       |    | 2  | 3  |    |    |    |    |    |    |
| Te      | 52            | 10                       |    | 2  | 4  |    |    |    |    |    |    |
| I       | 53            | 10                       |    | 2  | 5  |    |    |    |    |    |    |
| Xe      | 54            | 10                       |    | 2  | 6  |    |    |    |    |    |    |
| Cs      | 55            | 10                       |    | 2  | 6  |    |    | 1  |    |    |    |
| Ba      | 56            | 10                       |    | 2  | 6  |    |    | 2  |    |    |    |
| La      | 57            | 10                       |    | 2  | 6  | 1  |    | 2  |    |    |    |
| Ce      | 58            | 10                       | 1  | 2  | 6  | 1  |    | 2  |    |    |    |
| Pr      | 59            | 10                       | 3  | 2  | 6  |    |    | 2  |    |    |    |
| Nd      | 60            | 10                       | 4  | 2  | 6  |    |    | 2  |    |    |    |
| Pm      | 61            | 10                       | 5  | 2  | 6  |    |    | 2  |    |    |    |
| Sm      | 62            | 10                       | 6  | 2  | 6  |    |    | 2  |    |    |    |
| Eu      | 63            | 10                       | 7  | 2  | 6  |    |    | 2  |    |    |    |
| Gd      | 64            | 10                       | 7  | 2  | 6  | 1  |    | 2  |    |    |    |
| Tb      | 65            | 10                       | 9  | 2  | 6  |    |    | 2  |    |    |    |
| Dy      | 66            | 10                       | 10 | 2  | 6  |    |    | 2  |    |    |    |
| Ho      | 67            | 10                       | 11 | 2  | 6  |    |    | 2  |    |    |    |
| Er      | 68            | 10                       | 12 | 2  | 6  |    |    | 2  |    |    |    |
| Tm      | 69            | 10                       | 13 | 2  | 6  |    |    | 2  |    |    |    |
| Yb      | 70            | 10                       | 14 | 2  | 6  |    |    | 2  |    |    |    |
| Lu      | 71            | 10                       | 14 | 2  | 6  | 1  |    | 2  |    |    |    |
| Hf      | 72            | 10                       | 14 | 2  | 6  | 2  |    | 2  |    |    |    |
| Ta      | 73            | 10                       | 14 | 2  | 6  | 3  |    | 2  |    |    |    |
| W       | 74            | 10                       | 14 | 2  | 6  | 4  |    | 2  |    |    |    |
| Re      | 75            | 10                       | 14 | 2  | 6  | 5  |    | 2  |    |    |    |
| Os      | 76            | 10                       | 14 | 2  | 6  | 6  |    | 2  |    |    |    |
| Ir      | 77            | 10                       | 14 | 2  | 6  | 7  |    | 2  |    |    |    |
| Pt      | 78            | 10                       | 14 | 2  | 6  | 9  |    | 1  |    |    |    |
| Au      | 79            | 10                       | 14 | 2  | 6  | 10 |    | 1  |    |    |    |
| Hg      | 80            | 10                       | 14 | 2  | 6  | 10 |    | 2  |    |    |    |
| Tl      | 81            | 10                       | 14 | 2  | 6  | 10 |    | 2  | 1  |    |    |
| Pb      | 82            | 10                       | 14 | 2  | 6  | 10 |    | 2  | 2  |    |    |
| Bi      | 83            | 10                       | 14 | 2  | 6  | 10 |    | 2  | 3  |    |    |
| Po      | 84            | 10                       | 14 | 2  | 6  | 10 |    | 2  | 4  |    |    |
| At      | 85            | 10                       | 14 | 2  | 6  | 10 |    | 2  | 5  |    |    |
| Rn      | 86            | 10                       | 14 | 2  | 6  | 10 |    | 2  | 6  |    |    |
| Fr      | 87            | 10                       | 14 | 2  | 6  | 10 |    | 2  | 6  |    | 1  |
| Ra      | 88            | 10                       | 14 | 2  | 6  | 10 |    | 2  | 6  |    | 2  |
| Ac      | 89            | 10                       | 14 | 2  | 6  | 10 |    | 2  | 6  | 1  | 2  |
| Th      | 90            | 10                       | 14 | 2  | 6  | 10 |    | 2  | 6  | 2  | 2  |
| Pa      | 91            | 10                       | 14 | 2  | 6  | 10 | 2  | 2  | 6  | 1  | 2  |
| U       | 92            | 10                       | 14 | 2  | 6  | 10 | 3  | 2  | 6  | 1  | 2  |
| Np      | 93            | 10                       | 14 | 2  | 6  | 10 | 4  | 2  | 6  | 1  | 2  |
| Pu      | 94            | 10                       | 14 | 2  | 6  | 10 | 6  | 2  | 6  |    | 2  |
| Am      | 95            | 10                       | 14 | 2  | 6  | 10 | 7  | 2  | 6  |    | 2  |
| Cm      | 96            | 10                       | 14 | 2  | 6  | 10 | 7  | 2  | 6  | 1  | 2  |
| Bk      | 97            | 10                       | 14 | 2  | 6  | 10 | 9  | 2  | 6  |    | 2  |
| Cf      | 98            | 10                       | 14 | 2  | 6  | 10 | 10 | 2  | 6  |    | 2  |
| Es      | 99            | 10                       | 14 | 2  | 6  | 10 | 11 | 2  | 6  |    | 2  |
| Fm      | 100           | 10                       | 14 | 2  | 6  | 10 | 12 | 2  | 6  |    | 2  |
| Md      | 101           | 10                       | 14 | 2  | 6  | 10 | 13 | 2  | 6  |    | 2  |
| No      | 102           | 10                       | 14 | 2  | 6  | 10 | 14 | 2  | 6  |    | 2  |
| Lr      | 103           | 10                       | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 1  | 2  |
| Rf      | 104           | 10                       | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 2  | 2  |
| Db      | 105           | 10                       | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 3  | 2  |
| Sg      | 106           | 10                       | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 4  | 2  |
| Bh      | 107           | 10                       | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 5  | 2  |
| Hs      | 108           | 10                       | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 6  | 2  |
| Mt      | 109           | 10                       | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 7  | 2  |
| Ds      | 110           | 10                       | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 9  | 1  |



**Appendix IX. The Elements : Discoverers, Their Names and Symbols**

| Element             | Symbol    | Atomic Number | Date of Discovery | Discoverer and Nationality                                                        |
|---------------------|-----------|---------------|-------------------|-----------------------------------------------------------------------------------|
| Actinium            | Ac        | 89            | 1899              | A. Debierne (Fr.)                                                                 |
| Aluminium           | Al        | 13            | 1827              | F. Woehler (Ge.)                                                                  |
| Americium           | Am        | 95            | 1944              | A. Ghiorso (USA), R.A. James (USA)<br>G.T. Seaborg (USA), S.G. Thompson (USA)     |
| <b>Antimony</b>     | <b>Sb</b> | <b>51</b>     | <b>Ancient</b>    |                                                                                   |
| Argon               | Ar        | 18            | 1894              | Lord Rayleigh (GB), Sir William Ramsay (GB)                                       |
| Arsenic             | As        | 33            | 1250              | Albertus Magnus (Ge)                                                              |
| Astatine            | At        | 85            | 1940              | D.R. Corson (USA), K.R. MacKenzie (USA) E. Segre (USA)                            |
| Barium              | Ba        | 56            | 1808              | Sir Humphry Davy (GB)                                                             |
| Berkelium           | Bk        | 97            | 1950              | G.T. Seaborg (USA), S.G. Thompson (USA) A. Ghiorso (USA)                          |
| Beryllium           | Be        | 4             | 1828              | F. Woehler (Ge.), A.A.B. Bussy (Fr.)                                              |
| Bismuth             | Bi        | 83            | 1753              | Claude Geoffroy (Fr.)                                                             |
| Bohrium             | Bh        | 107           | 1976              | USA                                                                               |
| Boron               | B         | 5             | 1808              | Sir Humphry Davy (GB), J.L. Gay-Lussac (Fr.)<br>L.J. Thenard (Fr.)                |
| Bromine             | Br        | 35            | 1826              | A.J. Balard (Fr.)                                                                 |
| Cadmium             | Cd        | 48            | 1817              | Fr. Stromeyer (Ge.)                                                               |
| Calcium             | Ca        | 20            | 1808              | Sir Humphry Davy (GB)                                                             |
| Californium         | Cf        | 98            | 1950              | G.T. Seaborg (USA), S.G. Thompson (USA)<br>A. Ghiorso (USA), K. Street, Jr. (USA) |
| <b>Carbon</b>       | <b>C</b>  | <b>6</b>      | <b>Ancient</b>    |                                                                                   |
| Cerium              | Ce        | 58            | 1803              | J.J. Berzelius (Swe.), William Hisinger (Swe.)<br>M.H. Klaproth (Ge.)             |
| Cesium              | Cs        | 55            | 1860              | R. Bunsen (Ge.), G.R. Kirchhoff (Ge.)                                             |
| Chlorine            | Cl        | 17            | 1774              | K.W. Scheele (Swe.)                                                               |
| Chromium            | Cr        | 24            | 1797              | L.N. Vauquelin (Fr.)                                                              |
| Cobalt              | Co        | 27            | 1735              | G. Brandt (Ge.)                                                                   |
| <b>Copper</b>       | <b>Cu</b> | <b>29</b>     | <b>Ancient</b>    |                                                                                   |
| Curium              | Cm        | 96            | 1944              | G.T. Seaborg (USA), R.A. James (USA)<br>A. Ghiorso (USA)                          |
| <b>Darmstadtium</b> | <b>Ds</b> | <b>110</b>    | <b>2003</b>       | <b>Sigurd Hofmann (Ge)</b>                                                        |
| Dubnium             | Db        | 105           | 1970              |                                                                                   |
| Dysprosium          | Dy        | 66            | 1886              | Locoq de Boisbaudran (Fr.)                                                        |
| Einsteinium         | Es        | 99            | 1952              | A. Ghiorso (USA)                                                                  |
| Erbium              | Er        | 68            | 1843              | C.G. Mosander (Swe.)                                                              |
| Europium            | Eu        | 63            | 1896              | E. Demarcay (Fr.)                                                                 |
| Fermium             | Fm        | 100           | 1953              | A. Ghiorso (USA)                                                                  |
| Fluorine            | F         | 9             | 1886              | H. Moissan (Fr)                                                                   |
| Francium            | Fr        | 87            | 1939              | Marguerite Perey (Fr.)                                                            |
| Gadolinium          | Gd        | 64            | 1880              | J.C. Marignac (Fr.)                                                               |
| Gallium             | Ga        | 31            | 1875              | Lecoq de Boisbaudran (Fr.)                                                        |

| Element     | Symbol | Atomic Number | Date of Discovery | Discoverer and Nationality                                                                           |
|-------------|--------|---------------|-------------------|------------------------------------------------------------------------------------------------------|
| Germanium   | Ge     | 32            | 1886              | Clemens Winkler (Ge.)                                                                                |
| Gold        | Au     | 79            | Ancient           |                                                                                                      |
| Hafnium     | Hf     | 72            | 1923              | D. Coster (Du.), G. von Hevesey (H.)                                                                 |
| Helium      | He     | 2             | 1868              | P. Janssen (spectr) (Fr.), Sir William Ramsay (isolated) (GB)                                        |
| Hassium     | Hs     | 108           | 1984              | —                                                                                                    |
| Holmium     | Ho     | 67            | 1879              | P.T. Cleve (Swe.)                                                                                    |
| Hydrogen    | H      | 1             | 1766              | Sir Henry Cavendish (GB)                                                                             |
| Indium      | In     | 49            | 1863              | E. Reich (Ge.), T. Richter (Ge.)                                                                     |
| Iodine      | I      | 53            | 1811              | B. Courtois (Fr.)                                                                                    |
| Iridium     | Ir     | 77            | 1803              | S. Tennant (GB)                                                                                      |
| Iron        | Fe     | 26            | Ancient           |                                                                                                      |
| Krypton     | Kr     | 36            | 1898              | Sir William Ramsay (GB), M.W. Travers (GB)                                                           |
| Lanthanum   | La     | 57            | 1839              | C.G. Mosander (Swe.)                                                                                 |
| Lawrencium  | Lr     | 103           | 1961              | A. Ghiorso (USA), T. Sikkeland (USA)<br>A.E. Larsh (USA), R.M. Latimer (USA)                         |
| Lead        | Pb     | 82            | Ancient           |                                                                                                      |
| Lithium     | Li     | 3             | 1817              | A. Arfvedson (Swe)                                                                                   |
| Lutetium    | Lu     | 71            | 1907              | G. Urbain (Fr.), C.A. von Welsbach (Au.)                                                             |
| Magnesium   | Mg     | 12            | 1808              | Sir Humphry Davy (GB)                                                                                |
| Manganese   | Mn     | 25            | 1774              | J.G. Gahn (Swe.)                                                                                     |
| Mendelevium | Md     | 101           | 1955              | A. Ghiorso (USA), G.R. Choppin (USA)<br>G.T. Seaborg (USA), B.G. Harvey (USA)<br>S.G. Thompson (USA) |
| Meitnerium  | Mt     | 109           | 1982              | —                                                                                                    |
| Mercury     | Hg     | 80            | Ancient           |                                                                                                      |
| Molybdenum  | Mo     | 42            | 1778              | G.W. Scheele (Swe.)                                                                                  |
| Neodymium   | Nd     | 60            | 1885              | C.A. von Welsbach (Au.)                                                                              |
| Neon        | Ne     | 10            | 1898              | Sir William Ramsay (GB), M.W. Travers (GB)                                                           |
| Neptunium   | Np     | 93            | 1940              | E.M. McMillan (USA), P.H. Abelson (USA)                                                              |
| Nickel      | Ni     | 28            | 1751              | A.E. Cronstedt (Swe.)                                                                                |
| Niobium     | Nb     | 41            | 1801              | Charles Hatchett (GB)                                                                                |
| Nitrogen    | N      | 7             | 1772              | Daniel Rutherford (GB)                                                                               |
| Nobelium    | No     | 102           | 1958              | A. Ghiorso (USA), T. Sikkeland (USA)<br>J.R. Walton (USA), G.T. Seaborg (USA)                        |
| Osmium      | Os     | 76            | 1803              | S. Tennant (GB)                                                                                      |
| Oxygen      | O      | 8             | 1774              | Joseph Priestley (GB), C.W. Scheele (Swe.)                                                           |
| Palladium   | Pd     | 46            | 1803              | W.H. Wollaston (GB)                                                                                  |
| Phosphorus  | P      | 15            | 1669              | H. Brandt (Ge.)                                                                                      |
| Platinum    | Pt     | 78            | 1735              | A. De Ullao (Sp.)                                                                                    |
|             |        |               | 1741              | Charles Wood (GB)                                                                                    |
| Plutonium   | Pu     | 94            | 1940              | G.T. Seaborg (USA), E.M. McMillan (USA)<br>J.W. Kennedy (USA), A.C. Wahl (USA)                       |
| Polonium    | Po     | 84            | 1898              | Marie Curie (P.)                                                                                     |
| Potassium   | K      | 19            | 1807              | Sir Humphry Davy (GB)                                                                                |

| Element       | Symbol | Atomic Number | Date of Discovery | Discoverer and Nationality                                      |
|---------------|--------|---------------|-------------------|-----------------------------------------------------------------|
| Praseodymium  | Pr     | 59            | 1885              | C.A. von Welsbach (Au.)                                         |
| Promethium    | Pm     | 61            | 1945              | J.A. Marinsky (USA), L.E. Glendenin (USA)<br>C.D. Coryell (USA) |
| Protactinium  | Pa     | 91            | 1917              | O. Hahn (Ge.), L. Meitner (Au.)                                 |
| Radium        | Ra     | 88            | 1898              | Pierre and Marie Curie, (Fr.; P)                                |
| Radon         | Rn     | 86            | 1900              | F.E. Dorn (Ge.)                                                 |
| Rhenium       | Re     | 75            | 1925              | W. Noddack (Ge.), I. Tacke (Ge) Otto Berg (Ge)                  |
| Rhodium       | Rh     | 45            | 1804              | W.H. Wollaston (GB)                                             |
| Rubidium      | Rb     | 37            | 1861              | R.W. Bunsen (Ge.), G. Kirchhoff (Ge.)                           |
| Ruthenium     | Ru     | 44            | 1844              | K.K. Klaus (R.)                                                 |
| Rutherfordium | Rf     | 104           | 1965              | USA                                                             |
| Samarium      | Sm     | 62            | 1879              | Lecoq de Boisbaudran (Fr.)                                      |
| Scandium      | Sc     | 21            | 1879              | L.F. Nilson (Swe.)                                              |
| Seaborgium    | Sg     | 106           | 1976              | —                                                               |
| Selenium      | Se     | 34            | 1817              | J.J. Berzelius (Swe.)                                           |
| Silicon       | Si     | 14            | 1824              | J.J. Berzelius (Swe.)                                           |
| Silver        | Ag     | 47            | Ancient           |                                                                 |
| Sodium        | Na     | 11            | 1807              | Sir Humphry Davy (GB)                                           |
| Strontium     | Sr     | 38            | 1808              | Sir Humphry Davy (GB)                                           |
| Sulphur       | S      | 16            | Ancient           |                                                                 |
| Tantalum      | Ta     | 73            | 1802              | A.G. Ekeberg (Swe.)                                             |
| Technetium    | Tc     | 43            | 1937              | C. Perrier (I.)                                                 |
| Tellurium     | Te     | 52            | 1782              | E.J. Muller (Au.)                                               |
| Terbium       | Tb     | 65            | 1843              | C.G. Mosander (Swe.)                                            |
| Thallium      | Tl     | 81            | 1861              | Sir William Crookes (GB)                                        |
| Thorium       | Th     | 90            | 1828              | J.J. Berzelius (Swe.)                                           |
| Thulium       | Tm     | 69            | 1879              | P.T. Cleve (Swe.)                                               |
| Tin           | Sn     | 50            | Ancient           |                                                                 |
| Titanium      | Ti     | 22            | 1791              | W. Gregor (GB)                                                  |
| Tungsten      | W      | 74            | 1783              | J.J. and F. de Elhuyer (Sp.)                                    |
| Uranium       | U      | 92            | 1789              | M.H. Klaproth (Ge.)                                             |
|               |        |               | 1841              | E.M. Peligot (Fr.)                                              |
| Vanadium      | V      | 23            | 1801              | A.M. Del Rio (Sp.)                                              |
|               |        |               | 1830              | N.G. Sefstrom (Swe.)                                            |
| Xenon         | Xe     | 54            | 1898              | Sir William Ramsay (GB), M.W. Travers (GB)                      |
| Ytterbium     | Yb     | 70            | 1907              | G. Urbain (Fr.)                                                 |
| Yttrium       | Y      | 39            | 1843              | C.G. Mosander (Swe.)                                            |
| Zinc          | Zn     | 30            | 1746              | A.S. Marggraf (Ge.)                                             |
| Zirconium     | Zr     | 40            | 1789              | M.H. Klaproth (Ge.)                                             |

# Appendix X. Minerals with Metallic Luster

| Mineral (Formula)                                                                                                | Colour                                              | Crystal System | Uses and Other Properties                                                                          |
|------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------|----------------|----------------------------------------------------------------------------------------------------|
| <b>Graphite (C)</b>                                                                                              | black to grey                                       | hexagonal      | pencil lead, lubricants for locks, rods to control some small nuclear reactions, battery poles     |
| <b>Silver (Ag)</b>                                                                                               | silvery white, tarnishes to black                   | cubic          | coins, fillings for teeth, jewellery, silverplate, wires; malleable and ductile                    |
| <b>Galena (PbS)</b>                                                                                              | grey                                                | cubic          | source of lead, used in pipes, shields for X-rays, fishing equipment sinkers                       |
| <b>Gold (Au)</b>                                                                                                 | pale to golden yellow                               | cubic          | jewellery, money, gold leaf, fillings for teeth, medicines; does not tarnish                       |
| <b>Bornite [Cu<sub>5</sub>FeS<sub>4</sub>]</b>                                                                   | bronze, tarnishes to dark blue, purple              | tetragonal     | source of copper; called "peakcock ore" because of the purple shine when it tarnishes              |
| <b>Copper (Cu)</b>                                                                                               | copper red                                          | cubic          | coins, pipes, gutters, wire cooking utensils, jewellery, decorative plaques; malleable and ductile |
| <b>Chalcopyrite (CuFeS<sub>2</sub>)</b>                                                                          | brassy to golden yellow                             | tetragonal     | main ore of copper                                                                                 |
| <b>Chromite (FeCr<sub>2</sub>O<sub>4</sub>)</b>                                                                  | black or brown                                      | cubic          | ore of chromium, stainless steel, metallurgical bricks                                             |
| <b>Pyrrhotite (FeS)</b>                                                                                          | bronze                                              | hexagonal      | often found with pentlandite, an ore of nickel; may be magnetic                                    |
| <b>Haematite (specular) (Fe<sub>2</sub>O<sub>3</sub>)</b>                                                        | black or reddish brown                              | hexagonal      | source of iron; roasted in a blast furnace, converted to "pig" iron, made into steel               |
| <b>Magnetite (Fe<sub>3</sub>O<sub>4</sub>)</b>                                                                   | black                                               | cubic          | source of iron, naturally magnetic, called lodestone                                               |
| <b>Pyrite (FeS<sub>2</sub>)</b>                                                                                  | light, brassy, yellow                               | cubic          | source of iron, "fools's gold," alters to limonite                                                 |
| <b>Fluorite (CaF<sub>2</sub>)</b>                                                                                | colourless, white, blue, green, red, yellow, purple | cubic          | used in the manufacture of optical equipment; glows under ultraviolet light                        |
| <b>Limonite (hydrous iron oxides)</b>                                                                            | yellow, brown black                                 | —              | source of iron; weathers easily colouring matter of soils                                          |
| <b>Hornblende (CaNa(Mg, Al, Fe)<sub>5</sub>(Al, Si)<sub>2</sub>Si<sub>6</sub>O<sub>22</sub>(OH)<sub>2</sub>)</b> | green to black                                      | monoclinic     | will transmit light on thin edges; 6-sided cross section                                           |
| <b>Feldspar (orthoclase) (KAlSi<sub>3</sub>O<sub>8</sub>)</b>                                                    | colourless, white grey green and yellow             | monoclinic     | insoluble in acids; used in the manufacture of porcelain                                           |
| <b>Feldspar (plagioclase) (NaAlSi<sub>3</sub>O<sub>8</sub>) (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>)</b>    | grey, green white                                   | triclinic      | used in ceramics; striations present on some faces                                                 |
| <b>Augite (Ca, Na) (Mg, Fe, Al) (Al, Si)<sub>2</sub>O<sub>6</sub></b>                                            | black                                               | monoclinic     | square or 8-sided cross-section                                                                    |
| <b>Olivine ((Mg, Fe)<sub>2</sub>SiO<sub>4</sub>)</b>                                                             | olive green                                         | ortho-rhombic  | gemstones, refractory sand                                                                         |
| <b>Quartz (SiO<sub>2</sub>)</b>                                                                                  | colourless, various colours                         | hexagonal      | used in glass manufacture, electronic equipment, radios, computers, watches, gemstones             |
| <b>Garnet (Mg, Fe, Ca)<sub>3</sub> (Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>)</b>                              | deep yellow-red green, black                        | cubic          | used in jewellery, also used as an abrasive                                                        |
| <b>Topaz (Al<sub>2</sub>SiO<sub>4</sub>) (F, OH)<sub>2</sub></b>                                                 | white, pink yellow, pale blue, colourless           | ortho-rhombic  | valuable gemstone                                                                                  |
| <b>Corundum (Al<sub>2</sub>O<sub>3</sub>)</b>                                                                    | colourless, blue, brown green white, pink, red      | hexagonal      | gemstones; ruby is red, sapphire is blue; industrial abrasive                                      |

## Appendix XI. Mineral with Non-Metallic Lusture

| Mineral (Formula)                                                                               | Colour                                      | Crystal System | Uses and Other Properties                                                                                 |
|-------------------------------------------------------------------------------------------------|---------------------------------------------|----------------|-----------------------------------------------------------------------------------------------------------|
| <b>Talc</b> ( $\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}$ )                              | white, greenish                             | monoclinic     | easily cut with fingernail; used for talcum powder; soapstone is used in paper and for table tops         |
| <b>Bauxite</b><br>(hydrous aluminium compound)                                                  | grey, red, white, brown                     | —              | source of aluminium; used in paints, aluminium foil, and airplane parts                                   |
| <b>Kaolinite</b> ( $\text{Al}_4\text{Si}_2\text{O}_5(\text{OH})_4$ )                            | white, red, reddish brown, black            | triclinic      | clays; used in ceramics and in china dishes; common in most soils; often microscopic-sized particles      |
| <b>Gypsum</b> ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )                                     | colourless, grey, white, brown              | monoclinic     | used extensively in the preparation of plaster of Paris alabaster, and dry wall for building construction |
| <b>Sphalerite</b> ( $\text{ZnS}$ )                                                              | brown                                       | cubic          | main ore of zinc; used in paints, dyes, and medicine                                                      |
| <b>Sulphur</b> (S)                                                                              | yellow                                      | orthorhombic   | used in medicine, fungicides for plants, vulcanisation of rubber. Production of sulphuric acid            |
| <b>Muscovite</b><br>( $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ )                     | white, light grey, yellow, rose, green      | monoclinic     | occurs in large flexible plates, used as an insulator in electrical equipment, lubricant                  |
| <b>Biotite</b><br>( $\text{K}(\text{Mg}, \text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ ) | black to dark brown                         | monoclinic     | occurs in large flexible plates                                                                           |
| <b>Halite</b> ( $\text{NaCl}$ )                                                                 | colourless, red, white blue                 | cubic          | salt; very soluble in water; a preservative                                                               |
| <b>Calcite</b> ( $\text{CaCO}_3$ )                                                              | colourless, white pale, blue                | hexagonal      | fizzes when HCl is added; used in cement and other building materials                                     |
| <b>Dolomite</b> ( $\text{CaMg}(\text{CO}_3)_2$ )                                                | colourless, white, pink, green, grey, black | hexagonal      | concrete and cement, used as an ornamental building stone                                                 |

# JEE Main and Advanced (2017-10)

## Previous Years' Questions

### 1. Fundamental Concepts of Inorganic Chemistry

1. A stream of electrons from a heated filament was passed between two charged plates kept at a potential difference  $V$  esu. If  $e$  and  $m$  are charge and mass of an electron, respectively, then the value of  $h/\lambda$  (where,  $\lambda$  is wavelength associated with electron wave) is given by [JEE Main 2016]

- (a)  $2\text{ meV}$  (b)  $\sqrt{meV}$   
(c)  $\sqrt{2\text{ meV}}$  (d)  $meV$

Ans. (c) As you can see in options, energy term is mentioned hence, we have to find out relation between  $\frac{h}{\lambda}$  and energy. For this, we

shall use de-Broglie wavelength and kinetic energy term in eV.

de-Broglie wavelength for an electron ( $\lambda$ ) =  $\frac{h}{p}$

$$\Rightarrow p = \frac{h}{\lambda} \quad \dots(i)$$

Kinetic energy of an electron = eV

$$\text{As we know that, KE} = \frac{p^2}{2m}$$

$$\therefore \text{eV} = \frac{p^2}{2m}$$

$$\text{or } p = \sqrt{2meV} \quad \dots(ii)$$

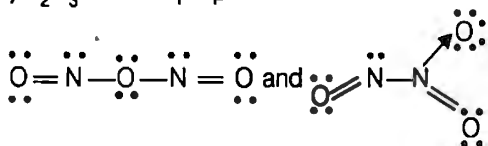
From equations (i) and (ii), we get  $\frac{h}{\lambda} = \sqrt{2meV}$

### 2. Chemical Bonding

1. The total number of lone pair of electrons in  $\text{N}_2\text{O}_2$  is

[JEE Advanced 2015, Integer Type]

Ans. (8)  $\text{N}_2\text{O}_3$  has two proposed structures.



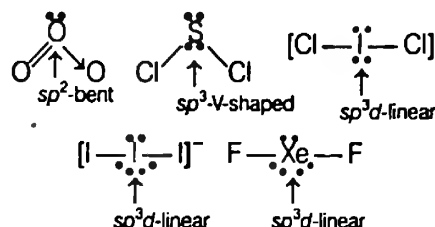
In both cases, number of lone pair of electrons are eight.

2. Among the triatomic molecules/ions  $\text{BeCl}_2$ ,  $\text{N}_3^-$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2^+$ ,  $\text{O}_3$ ,  $\text{SCl}_2$ ,  $\text{ICl}_2^-$ ,  $\text{I}_3^-$  and  $\text{XeF}_2$ , the total number of linear molecules/ion(s) where the hybridisation of the central atom does not have contribution from the  $d$ -orbital(s) is [atomic number of S = 16, Cl = 17, I = 53 and Xe = 54]

[JEE Advanced 2015, Integer Type]

Ans. (4)  $\text{Cl}-\underset{\uparrow sp}{\text{Be}}-\text{Cl}$   $\text{N}\equiv\underset{\uparrow sp}{\text{N}}\rightarrow\ddot{\text{N}}\cdot^-$   $\text{N}=\underset{\uparrow sp}{\text{N}}\rightarrow\ddot{\text{O}}\cdot$   $\text{O}=\underset{\uparrow sp}{\text{N}}=\text{O}$

All the above mentioned molecules/ions have  $sp$ -hybridised central atom and no lone pair at central atom, hence linear also. Others are :



[Although  $\text{ICl}_2^-$ ,  $\text{I}_3^-$  and  $\text{XeF}_2$  all also are linear but in them  $d$ -orbital contribute in hybridisation.]

3. Assuming  $2s$ - $2p$  mixing is not operative, the paramagnetic species among the following is

[JEE Advanced 2014, Single Option]

- (a)  $\text{Be}_2$  (b)  $\text{B}_2$   
(c)  $\text{C}_2$  (d)  $\text{N}_2$

Ans. (c) Assuming that no  $2s$ - $2p$  mixing takes place the molecular orbital electronic configuration can be written in the following sequence of energy levels of molecular orbitals

$$\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, \pi 2p_x = \pi 2p_y,$$

$$\pi^* 2p_x = \pi^* 2p_y, \sigma^* 2p_z$$

- (a)  $\text{Be}_2 \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2$  (diamagnetic)  
(b)  $\text{B}_2 \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2$  (diamagnetic)  
(c)  $\text{C}_2 \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2$

$$\pi 2p_x^1, \pi^* 2p_x^0, \pi 2p_y^1, \pi^* 2p_y^0 \text{ (paramagnetic)}$$

- (d)  $\text{N}_2 \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2, \pi 2p_y^2$  (diamagnetic)

4. Match the orbital overlap figures shown in List I with the description given in List II and select the correct answer using the code given below the lists.

[JEE Advanced 2014, Matching Type]

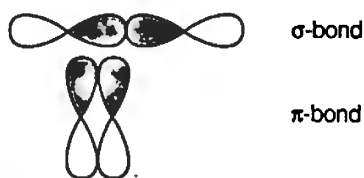
| List I |  | List II                        |
|--------|--|--------------------------------|
| P.     |  | 1. $p$ - $d$ $\pi$ antibonding |
| Q.     |  | 2. $d$ - $d$ $\sigma$ bonding  |

|    | List I | List II                     |
|----|--------|-----------------------------|
| R. |        | 3. $p-d \pi$ bonding        |
| S. |        | 4. $d-d \sigma$ antibonding |

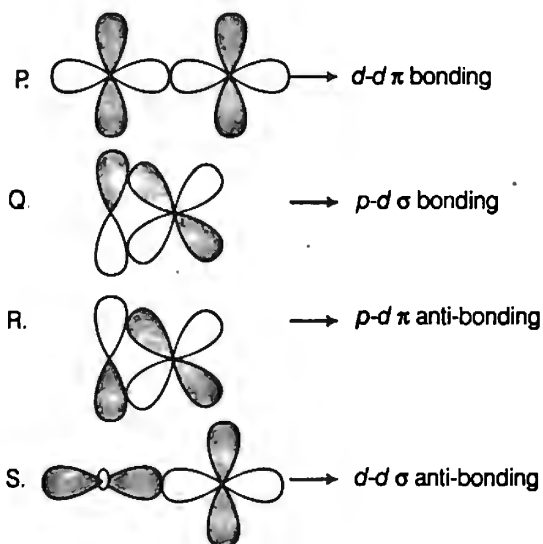
Codes

|     |   |   |   |   |     |   |   |   |   |
|-----|---|---|---|---|-----|---|---|---|---|
|     | P | Q | R | S |     | P | Q | R | S |
| (a) | 2 | 1 | 3 | 4 | (b) | 4 | 3 | 1 | 2 |
| (c) | 2 | 3 | 1 | 4 | (d) | 4 | 1 | 3 | 2 |

**Ans. (c)** This problem includes basic concept of bonding. It can be solved by using the concept of molecular orbital theory. Any orbital has two phases +ve and -ve. In the following diagram +ve phase is shown by darkening the lobes and -ve by without darkening the lobes. When two same phases overlap with each other it forms bonding molecular orbital otherwise antibonding.



On the basis of above two concepts correct matching can be done as shown below



$\therefore P \rightarrow 2, Q \rightarrow 3, R \rightarrow 1, S \rightarrow 4$

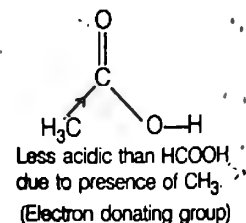
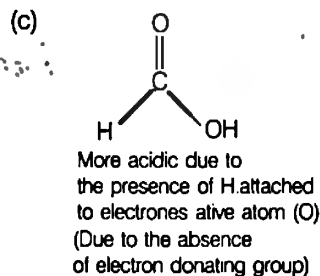
Hence, (c) is the correct option.

**5.** Hydrogen bonding plays a central role in the following phenomena [JEE Advanced 2014, More than One Option]

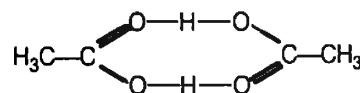
- (a) ice floats in water
- (b) higher Lewis basicity of primary amines than tertiary amines in aqueous solutions
- (c) formic acid is more acidic than acetic acid
- (d) dimerisation of acetic acid in benzene

**Ans. (a,b,c,d)** Ice floats in water due to the low density of ice as compare to water which is due to open cage like structure (formed by intermolecular H-bonding).

(b) Basic strength of  $RNH_2 > R_3N$ . It is also explained by hydrogen bonding.



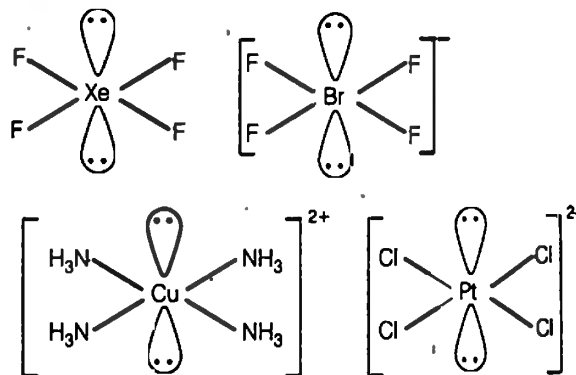
(d) Dimerisation of acetic acid in benzene is due to intermolecular hydrogen bonding.



**6.** A list of species having the formula  $XZ_4$  is given below  
 $XeF_4$ ,  $SF_4$ ,  $SiF_4$ ,  $BF_4^-$ ,  $BrF_4^-$ ,  $[Cu(NH_3)_4]^{2+}$ ,  $[FeCl_4]^{2-}$ ,  $[CoCl_4]^{2-}$  and  $[PtCl_4]^{2-}$ .

Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is [JEE Advanced 2014, Integer Type]

**Ans. (4)**  $XeF_4$ ,  $BrF_4^-$ ,  $[Cu(NH_3)_4]^{2+}$ ,  $[PtCl_4]^{2-}$  are square planar as shown below



**7.** Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule  $B_2$  is [JEE Advanced 2010, Single Option]

- (a) 1 and diamagnetic
- (b) 0 and diamagnetic
- (c) 1 and paramagnetic
- (d) 0 and paramagnetic

**Ans. (a)** For molecules lighter than  $O_2$ , the increasing order of energies of molecular orbitals is :

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \left[ \begin{matrix} \pi 2p_y \\ \pi 2p_z \end{matrix} \right] < \sigma 2p_x$$

Where,  $\pi 2p_y$  and  $\pi 2p_z$  are degenerate molecular orbitals, first singly occupied and then pairing starts if Hund's rule is obeyed. If Hund's rule is violated in  $B_2$ , electronic arrangement would be :

$$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \left[ \begin{matrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{matrix} \right]$$

No-unpaired electron-diamagnetic.

Bond-order

$$= \frac{\text{bonding electrons} - \text{antibonding electrons}}{2} = \frac{6 - 4}{2} = 1$$

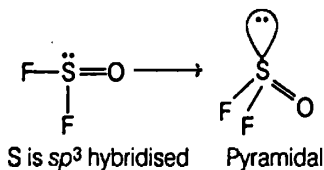
## Previous Years' Questions (2017-10)

8. The species having pyramidal shape is

[IIT JEE 2010, Single Option]

- (a)  $\text{SO}_3$  (b)  $\text{BrF}_3$   
(c)  $\text{SiO}_3^{2-}$  (d)  $\text{OSF}_2$

Ans. (d)



$\text{SO}_3$  is planar (S is  $sp^2$  hybridised),  $\text{BrF}_3$  is T-shaped and  $\text{SiO}_3^{2-}$  is planar (Si is  $sp^2$  hybridised).

9. Based on VSEPR theory, the number of  $90^\circ$  F—Br—F angles in  $\text{BrF}_5$  is

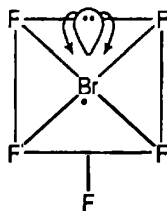
[IIT JEE 2010, Integer Type]

- (a) 0 (b) 1  
(c) 2 (d) 3

Ans. (d) In  $\text{BrF}_5$  number of electrons =  $6(1p + 1bp)$

So, the structure is supported to be square pyramidal but will be distorted because of additional  $lp-bp$  interaction.

Additional  $lp-bp$  interaction reduced the all bond angle and do not let any angle to be  $90^\circ$ .



10. The correct statement for the molecule,  $\text{CsI}_3$  is

[JEE Main 2014]

- (a) it is a covalent molecule  
(b) it contains  $\text{Cs}^+$  and  $\text{I}_3^-$  ions  
(c) it contains  $\text{Cs}^{3+}$  and  $\text{I}^-$  ions  
(d) it contains  $\text{Cs}^+$ ,  $\text{I}^-$  and lattice  $\text{I}_2$  molecule

Ans. (b)  $\text{CsI}_3$  is an ionic compound. It consists of  $\text{Cs}^+$  (cation) and  $\text{I}_3^-$  (anion) ions.  $\text{I}_3^-$  ion is made up of  $\text{I}_2$  and  $\text{I}^-$  which is linear in shape.

11. Which one of the following molecules is expected to exhibit diamagnetic behaviour?

[JEE Main 2013]

- (a)  $\text{C}_2$  (b)  $\text{N}_2$   
(c)  $\text{O}_2$  (d)  $\text{S}_2$

Ans. (a, b) MOEC of  $\text{C}_2(6 + 6 = 12) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2, \pi 2p_y^2$

Since, all the electrons are paired, it is a diamagnetic species.

MOEC of  $\text{N}_2(7 + 7 = 14) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2, \pi 2p_y^2$

It is also a diamagnetic species because of the absence of unpaired electrons.

MOEC of  $\text{O}_2(8 + 8 = 16)$

Or

$$= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2$$

$$= \pi 2p_y^2, \pi 2p_x^1, \pi 2p_y^1$$

Due to the presence of two unpaired electrons  $\text{O}_2$  and also  $\text{S}_2$  both are paramagnetic molecules.

12. In which of the following pairs of molecules/ions both the species are not likely to exist?

[JEE Main 2013]

- (a)  $\text{H}_2^+, \text{He}_2^{2-}$  (b)  $\text{H}_2^-, \text{He}_2^{2-}$   
(c)  $\text{H}_2^{2+}, \text{He}_2$  (d)  $\text{H}_2^-, \text{He}_2^{2+}$

Ans. (c) Species having zero or negative bond order do not exist.

$$\text{H}_2^+ (1 + 1 - 2 = 0) = \sigma 1s^0, \text{Bond order} = 0$$

$$\text{He}_2 (2 + 2 = 4) = \sigma 1s^2, \sigma^* 1s^2$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 2}{2} = 0$$

So, both  $\text{H}_2^{2+}$  and  $\text{He}_2$  do not exist.

13. Stability of the species  $\text{Li}_2, \text{Li}_2^-$  and  $\text{Li}_2^+$  increases in the order of

[JEE Main 2013]

- (a)  $\text{Li}_2 < \text{Li}_2^+ < \text{Li}_2^-$  (b)  $\text{Li}_2^- < \text{Li}_2^+ < \text{Li}_2$   
(c)  $\text{Li}_2 < \text{Li}_2^- < \text{Li}_2^+$  (d)  $\text{Li}_2^- < \text{Li}_2 < \text{Li}_2^+$

Ans. (b)  $\text{Li}_2 (3 + 3 = 6) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{4 - 2}{2} = 1$$

$$\text{Li}_2^+ (3 + 3 - 1 = 5) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^1$$

$$\text{Bond order} = \frac{3 - 2}{2} = \frac{1}{2} = 0.5$$

$$\text{Li}_2^- (3 + 3 + 1 = 7) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^1$$

$$\text{Bond order} = \frac{4 - 3}{2} = \frac{1}{2} = 0.5$$

Stability order is  $\text{Li}_2 > \text{Li}_2^+ > \text{Li}_2^-$  (because  $\text{Li}_2^-$  have more number of electrons in antibonding orbital).

14. The molecule having smallest bond angle is [AIEEE 2012]

- (a)  $\text{NCl}_3$  (b)  $\text{AsCl}_3$   
(c)  $\text{SbCl}_3$  (d)  $\text{PCl}_3$

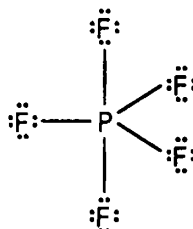
Ans. (c)  $\text{NCl}_3, \text{PCl}_3, \text{AsCl}_3, \text{SbCl}_3, \text{BiCl}_3$

As electronegativity of central atom decreases and size of central atom increases therefore, bond angle decreases. According to question,  $\text{SbCl}_3$  has lowest bond angle.

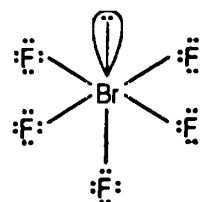
15. Which of the following pair is not isostructural?

- (a)  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$  (b)  $\text{PCl}_3$  and  $\text{SiCl}_4$  [AIEEE 2012]  
(c)  $\text{PF}_5$  and  $\text{BrF}_5$  (d)  $\text{AlF}_6^{3-}$  and  $\text{SF}_6$

Ans. (c) Compounds having same structure are known as isostructural. The structure of compound depends upon number of valence electrons. Except  $\text{PF}_5$  and  $\text{BrF}_5$  (where number of valence electrons are 40 and 42) all have same valence electrons and are isostructural.



$sp^3d$  hybridisation of P and trigonal bipyramidal structural



Six pairs of electrons around  $sp^3d^2$  hybridisation of Br atom square pyramidal



**Ans. (c)** Ionisation energy increases along a period from left to right and decreases down a group. The position of given elements in the periodic table is as group

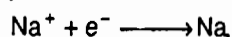
|       |    |    |    |
|-------|----|----|----|
| group | 2  | 16 | 18 |
|       | Ca | S  | Ar |
|       | Ba | Se |    |

The order of increasing  $\Delta H_{IE}$  is  
Ba < Ca < Se < S < Ar.

5. The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of  $\text{Na}^+$  will be [JEE Main 2013]

(a) -2.55 eV (b) -5.1 eV  
(c) -102 eV (d) +2.55 eV

Ans. (b)  $\text{Na} \longrightarrow \text{Na}^+ + e^- \text{ IE}_1$



Electron gain enthalpy of  $\text{Na}^+$

Because reaction is reverse so,  $\Delta H_{eg} = -5.1 \text{ eV}$

6. The increasing order of the ionic radii of the given isoelectronic species is [AIEEE 2012]

(a)  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{S}^{2-}$   
(b)  $\text{S}^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$   
(c)  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{S}^{2-}$   
(d)  $\text{K}^+$ ,  $\text{S}^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$

Ans. (c) For the case of isoelectronic species, the size of ionic radii decreases as the atomic number increases.  $\left(\Omega_n \propto \frac{1}{Z}\right)$

7. The correct order of electron gain enthalpy with negative sign of F, Cl, Br and I, having atomic number 9, 17, 35 and 53 respectively, is [AIEEE 2011]

(a)  $\text{I} > \text{Br} > \text{Cl} > \text{F}$   
(b)  $\text{F} > \text{Cl} > \text{Br} > \text{I}$   
(c)  $\text{Cl} > \text{F} > \text{Br} > \text{I}$   
(d)  $\text{Br} > \text{Cl} > \text{I} > \text{F}$

Ans. (c) As we move from top to bottom, size increases but force of attraction for the added extra electron decreases, thus electron gain enthalpy decreases.

The order should  $\text{F} < \text{Cl} < \text{Br} < \text{I}$

but actual order is  $\text{Cl} > \text{F} > \text{Br} > \text{I}$  because extra  $e^-$  added to  $2p$ -orbital of F is repelled to a greater extent than  $3p$ -orbital of Cl atom due to shielding effect of  $3d$ -orbital hence F has more electron affinity than Cl.

8. The correct sequence which shows decreasing order of the ionic radii of the elements is [AIEEE 2010]

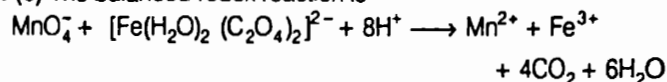
(a)  $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+ > \text{F}^- > \text{O}^{2-}$   
(b)  $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+} > \text{O}^{2-} > \text{F}^-$   
(c)  $\text{Na}^+ > \text{F}^- > \text{Mg}^{2+} > \text{O}^{2-} > \text{Al}^{3+}$   
(d)  $\text{O}^{2-} > \text{F}^- > \text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$

Ans. (d) For isoelectronic species, higher the nuclear charge hence lower the size.  $\left(\Omega_n \propto \frac{1}{Z}\right)$

## 4. Oxidation-Reduction

1. In dilute aqueous  $\text{H}_2\text{SO}_4$  the complex diaquadioxalatoferrate (II) is oxidised by  $\text{MnO}_4^-$ . For this reaction, the ratio of the rate of change of  $[\text{H}^+]$  to the rate of change of  $[\text{MnO}_4^-]$  is [JEE Advanced 2015, Integer Type]

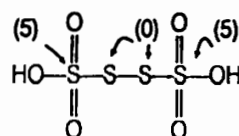
Ans. (8) The balanced redox reaction is



$$\Rightarrow \frac{r[\text{H}^+]}{r[\text{MnO}_4^-]} = \frac{8}{1} = 81111$$

2. The difference in the oxidation numbers of the two types of sulphur atoms in  $\text{Na}_2\text{S}_4\text{O}_6$  is [IIT JEE 2011, Integer Type]

Ans. (5)  $\text{Na}_2\text{S}_4\text{O}_6$  is a salt of  $\text{H}_2\text{S}_4\text{O}_6$  which has the following structure



$\Rightarrow$  Difference in oxidation number of two types of sulphur = 5

3. Among the following, the number of elements showing only one non-zero oxidation state is O, Cl, F, N, P, Sn, Ti, Na, Ti. [IIT JEE 2010, Integer Type]

Ans. (2) Only F and Na show only one non-zero oxidation state.

O = -1, -2, +2; Cl = -1 to +7

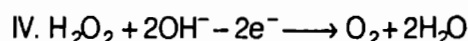
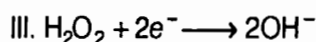
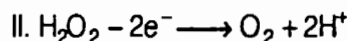
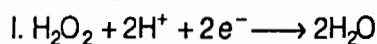
N = -3 to +5; P = -3 to +5

Sn = +2, +4; Ti = +1, +3 (rare but does exist)

Ti = +2, +3, +4

F, being the most electronegative element, exhibits only -1 state, and, Na being an alkali metal, exhibits only +1, state.

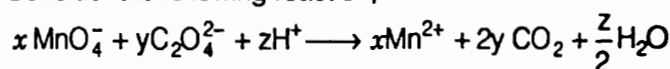
4. In which of the following reactions,  $\text{H}_2\text{O}_2$  acts as a reducing agent? [JEE Main 2014]



(a) I and II (b) III and IV (c) I and III (d) II and IV

Ans. (d) In II and IV,  $\text{H}_2\text{O}_2$  acts as a reducing agent as it is oxidised by losing two electrons in each.

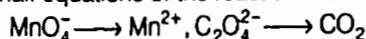
5. Consider the following reaction,



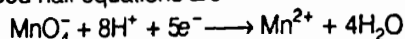
The values of x, y and z in the reaction respectively are [JEE Main 2013]

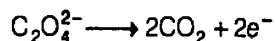
(a) 5, 2 and 16 (b) 2, 5 and 8  
(c) 2, 5 and 16 (d) 5, 2 and 8

Ans. (c) The half equations of the reaction are

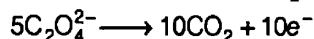
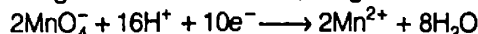


The balanced half equations are

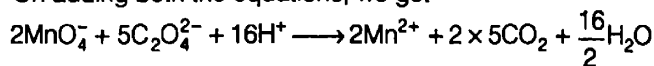




On equating number of electrons, we get



On adding both the equations, we get



Thus, x, y and z are 2, 5 and 16 respectively.

## 5. Radioactivity

1. In the nuclear transmutation  ${}^9_4\text{Be} + X \longrightarrow {}^8_4\text{Be} + Y$

(X, Y) is (are) [JEE Advanced 2013, More than One Option]

(a) ( $\gamma$ , n) (b) ( $\rho$ , D)

(c) (n, D) (d) ( $\gamma$ ,  $\rho$ )

Ans. (a, b) Plan  ${}^9_4\text{Be} + {}^b_aX \longrightarrow {}^8_4\text{Be} + {}^d_cY$

Atomic number same  $4 + a = 4 + c$

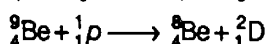
$$9 + b = 8 + d$$

$$\text{If } X = {}^0_0\gamma \quad a = 0; b = 0$$

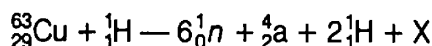
$$Y = {}^1_0n \quad c = 0; d = 1$$

$$\text{If } X = {}^1_1\rho \quad a = 1; b = 1$$

$$Y = {}^2_1\text{D} \quad c = 1; d = 2$$



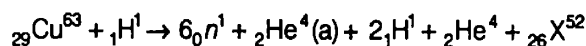
2. The Periodic Table consists of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element X as shown below.



To which group, element X belongs in the Periodic Table?

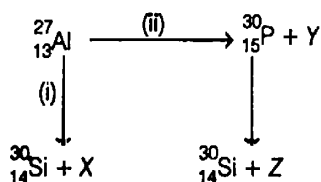
[JEE Advanced 2012, Integer Type]

Ans. (8) Balancing the given nuclear reaction in terms of atomic number (charge) and mass number gives :



The atomic number 26 correspond to transition metal "Fe" which belongs to 8th group of modern Periodic Table.

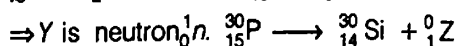
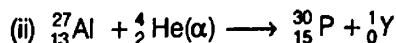
3. Bombardment of aluminium by  $\alpha$ -particle leads to its artificial disintegration in two ways, (i) and (ii) as shown. Products X, Y and Z respectively are,



[IIT JEE 2011, Single Option]

- (a) proton, neutron, positron (b) neutron, positron, proton  
(c) proton, positron, neutron (d) positron, proton, neutron

Ans. (a) (i)  ${}^{27}_{13}\text{Al} + {}^4_2\text{He}(\alpha) \longrightarrow {}^{30}_{14}\text{Si} + {}^1_1\text{X} \Rightarrow \text{X is proton } {}^1_1\text{H}$

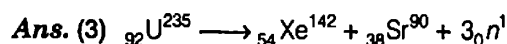


4. The number of neutrons emitted when  ${}^{235}_{92}\text{U}$  undergoes controlled nuclear fission to  ${}^{142}_{54}\text{Xe}$  and  ${}^{90}_{38}\text{Sr}$  is

[IIT JEE 2010, Integer Type]

- (a) 1  
(c) 3

- (b) 2  
(d) 4



## 6. Chemical Equations and Reactions

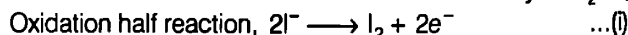
1. For the reaction,  $\text{I}^- + \text{ClO}_3^- + \text{H}_2\text{SO}_4 \longrightarrow \text{Cl}^- + \text{HSO}_4^- + \text{I}_2$  the correct statement(s) in the balanced equation is/are [JEE Advanced 2014, More than One Option]

- (a) stoichiometric coefficient of  $\text{HSO}_4^-$  is 6  
(b) iodide is oxidised  
(c) sulphur is reduced  
(d)  $\text{H}_2\text{O}$  is one of the products

Ans. (a, b, d) Write both half-cell reactions, i.e., oxidation half-cell reaction and reduction half-cell reaction.

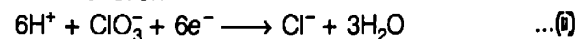
Then balance both the equations.

Now determine the correct value of stoichiometry of  $\text{H}_2\text{SO}_4$ .



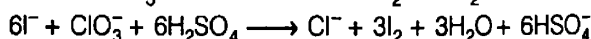
Here,  $\text{I}^-$  is converted into  $\text{I}_2$ . Oxidation number of I is increasing from -1 to 0 hence, this is a type of oxidation reaction.

Reduction half reaction



Here,  $\text{H}_2\text{O}$  releases as a product. Hence, option (d) is correct.

Multiplying Eq. (i) by 3 and adding in Eq. (ii)



Stoichiometric coefficient of  $\text{HSO}_4^-$  is 6.

## 7. Volumetric

1. A student performs a titration with different burettes and finds titre values of 25.2 mL, 25.25 mL, and 25.0 mL. The number of significant figures in the average titre value is

[IIT JEE 2010, Integer Type]

Ans. (3) Average titre value is 25.15, but the number of significant figure cannot be greater than the same in either of them being manipulated. So,  $25.15 \approx 252$ . Thus, the number of significant figure is 3.

2. Among  $\text{PbS}$ ,  $\text{CuS}$ ,  $\text{HgS}$ ,  $\text{MnS}$ ,  $\text{Ag}_2\text{S}$ ,  $\text{NiS}$ ,  $\text{CoS}$ ,  $\text{Bi}_2\text{S}_3$  and  $\text{SnS}_2$  the total number of black coloured sulphides is

[JEE Advanced 2014, Integer Type]

Ans. (7) From qualitative analysis of the different metal ions it is found that

$\text{PbS}$ ,  $\text{CuS}$ ,  $\text{HgS}$ ,  $\text{Ag}_2\text{S}$ ,  $\text{NiS}$ ,  $\text{CoS}$  are black coloured

$\text{MnS}$ —dirty pink/buff coloured,  $\text{SnS}_2$ —yellow coloured and

$\text{Bi}_2\text{S}_3$

Hence, correct integer is (7).

3. Upon treatment with ammoniacal  $\text{H}_2\text{S}$ , the metal ion that precipitates as a sulphide is

[JEE Advanced 2013, More Than One Option]

- (a) Fe (III) (b) Al (III) (c) Mg (II) (d) Zn (II)



## 8. s-Block Elements - The Alkali Metals

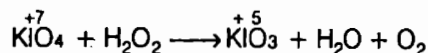
1. Hydrogen peroxide in its reaction with  $\text{KIO}_4$  and  $\text{NH}_2\text{OH}$  respectively, is acting as a [JEE Advanced 2014, Single Option]

- (a) reducing agent, oxidising agent  
(b) reducing agent, reducing agent  
(c) oxidising agent, oxidising agent  
(d) oxidising agent, reducing agent

**Ans. (a) Oxidant** Oxidant increases the oxidation number of the species with which it is reacted.

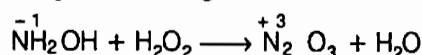
**Reductant** Reductant decreases the oxidation number of the species with which it is reacted.

$\text{H}_2\text{O}_2$  reacts with  $\text{KIO}_4$  in the following manner



On reaction of  $\text{KIO}_4$  with  $\text{H}_2\text{O}_2$ , oxidation state of I changes from +7 to +5 i.e., decreases. Thus,  $\text{KIO}_4$  gets reduced hence,  $\text{H}_2\text{O}_2$  is a reducing agent here.

With  $\text{NH}_2\text{OH}$ , it given following reaction



In the above reaction, oxidation state of N changes from -1 to +3. Here, oxidation number increases hence,  $\text{H}_2\text{O}_2$  is acting as an oxidising agent here.

Hence, (a) is the correct choice.

## 9. s-Block Elements - The Alkaline Earth Metals

1. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy? [JEE Main 2015]

- (a)  $\text{CaSO}_4$  (b)  $\text{BeSO}_4$   
(c)  $\text{BaSO}_4$  (d)  $\text{SrSO}_4$

**Ans. (b)** As we move down the group, size of metal increases. Be has lower size while  $\text{SO}_4^{2-}$  has bigger size, that's why  $\text{BeSO}_4$  breaks easily and lattice energy becomes smaller but due to lower size of Be, water molecules are gathered around and hence hydration energy increases.

On the other hand, rest metals i.e. Ca, Ba, Sr have bigger size and that's why lattice energy is greater than hydration energy.

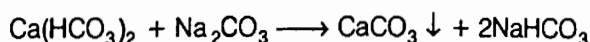
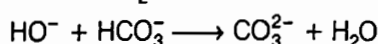
**Time Saving Technique** In the question of finding hydration energy only check the size of atom. Smaller sized atom has more hydration energy.

Thus, in this question Be is placed upper most in the group has lesser size and not comparable with the size of sulphates. Hence,  $\text{BeSO}_4$  is the right response.

2. The reagent(s) used for softening the temporary hardness of water is(are) [IIT JEE 2010, More than One Option]

- (a)  $\text{Ca}_3(\text{PO}_4)_2$  (b)  $\text{Ca}(\text{OH})_2$   
(c)  $\text{Na}_2\text{CO}_3$  (d)  $\text{NaOCl}$

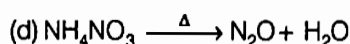
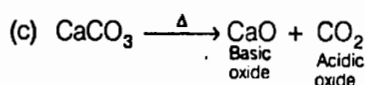
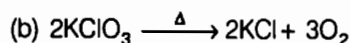
**Ans. (b,c,d)**  $\text{Ca}(\text{OH})_2 + \text{Ca}(\text{HCO}_3)_2 \longrightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$   
 $\text{NaOCl} + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{HOCl}$  (Clark's method)



3. Which of the following on thermal decomposition yields a basic as well as acidic oxide? [AIEEE 2012]

- (a)  $\text{NaNO}_3$  (b)  $\text{KClO}_3$   
(c)  $\text{CaCO}_3$  (d)  $\text{NH}_4\text{NO}_3$

**Ans. (c)** (a)  $2\text{NaNO}_3 \xrightarrow{\Delta} 2\text{NaNO}_2 + \text{O}_2$



## 10. Hydrogen and Its Compounds

1. Which of the following combination will produce  $\text{H}_2$  gas? [JEE Advanced 2017, Only One Correct Option]

- (a) Fe metal and conc.  $\text{HNO}_3$   
(b) Cu metal and conc.  $\text{HNO}_3$   
(c) Au metal and  $\text{NaCN}(\text{aq})$  in the presence of air  
(d) Zn metal and  $\text{NaOH}(\text{aq})$

**Ans. (d)**  $\underset{\text{Amphoteric}}{\text{Zn}} + 2\text{NaOH} \longrightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2$

2. Which one of the following statements about water is false? [JEE Main 2016]

- (a) Water can act both as an acid and as a base  
(b) There is extensive intramolecular hydrogen bonding in the condensed phase  
(c) Ice formed by heavy water sinks in normal water  
(d) Water is oxidised to oxygen during photosynthesis

**Ans. (b)** There is extensive intermolecular H-bonding in the condensed phase.

3. From the following statements regarding  $\text{H}_2\text{O}_2$ , choose the incorrect statement. [JEE Main 2015]

- (a) It can act only as an oxidising agent  
(b) It decomposed on exposure to light  
(c) It has to be stored in plastic or wax lined glass bottles in dark  
(d) It has to be kept away from dust

**Ans. (a)**  $\text{H}_2\text{O}_2$  acts as an oxidising as well as reducing agent, because oxidation number of oxygen in  $\text{H}_2\text{O}_2$  is -1. So, it can be oxidised to oxidation state 0 or reduced to oxidation state -2.

$\text{H}_2\text{O}_2$  decomposes on exposure to light. So, it has to be stored in plastic or wax lined glass bottles in dark for the prevention of exposure. It also has to be kept away from dust.

4.  $\text{Fe}^{3+}$  is reduced to Fe by using [JEE Advanced 2015, Only One Correct Option]

- (a)  $\text{H}_2\text{O}_2$  in the presence of  $\text{NaOH}$   
(b)  $\text{Na}_2\text{O}_2$  in water  
(c)  $\text{H}_2\text{O}_2$  in the presence of  $\text{H}_2\text{SO}_4$   
(d)  $\text{Na}_2\text{O}_2$  in the presence of  $\text{H}_2\text{SO}_4$

**Ans. (c)**  $\text{H}_2\text{O}_2$  in alkaline medium acts as reducing agent, reduces  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . In acidic medium the same  $\text{H}_2\text{O}_2$  oxidises  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ .

5. Very pure hydrogen (99.9%) can be made by which of the following processes? [AIEEE 2012]

(a) Reaction of methane with steam  
(b) Mixing natural hydrocarbons of high molecular weight  
(c) Electrolysis of water  
(d) Reaction of salts like hydrides with water

Ans. (c) On large scale, very pure hydrogen (>99.95%) can be obtained by electrolysis of water containing barium hydroxide in small amounts between nickel electrodes.

## 11. p-Block Elements - Boron Family [Group 13]

1. The increasing order of atomic radii of the following Group 13 elements is [JEE Advanced 2016, Single Option Correct]

(a)  $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$  (b)  $\text{Ga} < \text{Al} < \text{In} < \text{Tl}$   
(c)  $\text{Al} < \text{In} < \text{Ga} < \text{Tl}$  (d)  $\text{Al} < \text{Ga} < \text{Tl} < \text{In}$

Ans. (b) Due to poor shielding of  $d$ -orbital in Ga, atomic radius of Ga is smaller than that of Al. Thus,

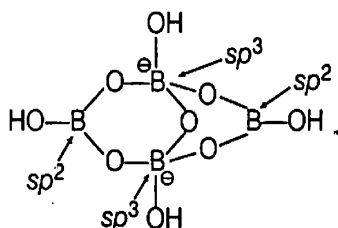


2. The crystalline form of borax has

[JEE Advanced 2016, One or More Than One Correct Option]

(a) tetranuclear  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$  unit  
(b) all boron atoms in the same plane  
(c) equal number of  $sp^2$  and  $sp^3$  hybridised boron atoms  
(d) one terminal hydroxide per boron atom

Ans. (a, c, d)  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  (borax) is actually made of two tetrahedral and two triangular units, and is actually written as  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 5\text{H}_2\text{O}$ .



(a) Thus, correct.  
(b) Boron atoms are in different planes thus, incorrect.  
(c) Two  $sp^2$  and two  $sp^3$ -hybridised B atoms thus, correct.  
(d) Each boron has one  $-\text{OH}$  group thus, correct.

3. Three moles of  $\text{B}_2\text{H}_6$  are completely reacted with methanol. The number of moles of boron containing product formed is [JEE Advanced 2015, Integer Type]

Ans. (6)  $\text{B}_2\text{H}_6 + 6 \text{CH}_3\text{OH} \longrightarrow 2[\text{B}(\text{OCH}_3)_3] + 6\text{H}_2$   
Therefore, from 3 moles of  $\text{B}_2\text{H}_6$ , 6 moles of  $\text{B}(\text{OCH}_3)_3$  will be

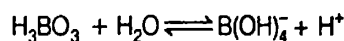
4. The correct statement(s) for orthoboric acid is/are

[JEE Advanced 2014, More than One Option]

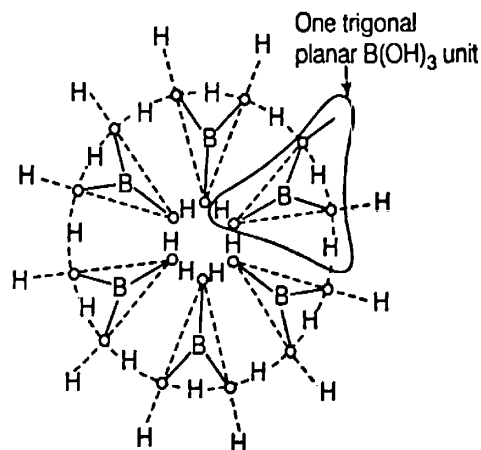
(a) it behaves as a weak acid in water due to self ionisation

(b) acidity of its aqueous solution increases upon addition of ethylene glycol  
(c) it has a three dimensional structure due to hydrogen bonding  
(d) it is a weak electrolyte in water

Ans. (b, d) For option (a) It does not undergo self ionisation in water but accepts an electron pair from water, so it behaves as weak monobasic acid

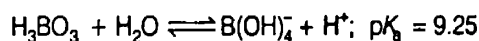


Hence, (a) is incorrect.



For option (b) When treated with 1, 2-dihydroxy or polyhydroxy compounds, they form chelate (ring complex) which effectively remove  $[\text{B}(\text{OH})_4]^-$  species from solution and thereby produce maximum number of  $\text{H}_3\text{O}^+$  or  $\text{H}^+$  ions, i.e. results in increased acidity. For option (c) Boric acid crystallises in a layer structure in which planar triangular  $\text{BO}_3^{2-}$  ions are bonded together through hydrogen bonds.

For option (d) In water the  $pK_a$  value of  $\text{H}_3\text{BO}_3$  is 9.25.



So, it is a weak electrolyte in water.

5. The value of  $n$  in the molecular formula  $\text{Be}_n\text{Al}_2\text{Si}_6\text{O}_{18}$  is

[IIT JEE 2010, Integer Type]

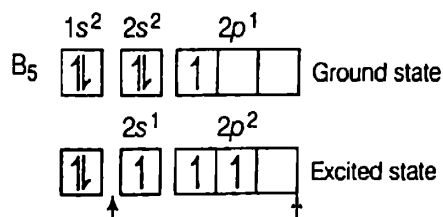
Ans. (3)  $\text{Be}_n\text{Al}_2\text{Si}_6\text{O}_{18}$ ,  $2n + 6 + 24 - 36 = 0$   
 $\Rightarrow n = 3$

6. Boron can't form which one of the following anions?

[AIEEE 2011]

(a)  $\text{BF}_6^{3-}$  (b)  $\text{BH}_4^-$   
(c)  $\text{B}(\text{OH})_4^-$  (d)  $\text{BO}_2^-$

Ans. (a)



Fourth lone pair is accommodated in this empty orbital

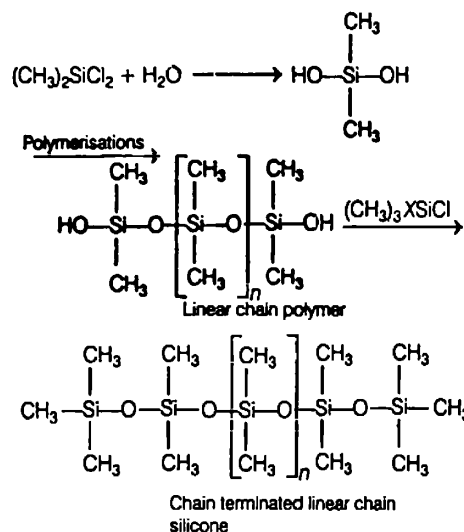
Maximum covalency = 4

## 12. Group 14 [IVA-The Carbon Family]

1. Under hydrolysis conditions, the compounds used for preparation of linear polymer and for chain termination, respectively are [JEE Advanced 2015, Single Option]

(a)  $\text{CH}_3\text{SiCl}_3$  and  $\text{Si}(\text{CH}_3)_4$  (b)  $(\text{CH}_3)_2\text{SiCl}_2$  and  $(\text{CH}_3)_3\text{SiCl}$   
 (c)  $(\text{CH}_3)_3\text{SiCl}_2$  and  $\text{CH}_3\text{SiCl}_3$  (d)  $\text{SiCl}_4$  and  $(\text{CH}_3)_3\text{SiCl}$

Ans. (b)



2. With respect to graphite and diamond, which of the statement(s) given below is (are) correct?

[JEE Advanced 2012, More than One Option]

(a) Graphite is harder than diamond.  
 (b) Graphite has higher electrical conductivity than diamond.  
 (c) Graphite has higher thermal conductivity than diamond.  
 (d) Graphite has higher C—C bond order than diamond.

Ans. (b,d) Diamond has a three dimensional network structure, a hard substance where graphite is soft due to layered structure.

In graphite, only three valence electrons are involved in bonding and one electron remains free giving electrical conductivity. In diamond, all the four valence electrons are covalently bonded hence, insulator. Diamond is better thermal conductor than graphite. Electrical conductivity is due to availability of free electrons, thermal conduction is due to transfer of thermal vibrational energy from one atom to another atom.

A compact and precisely aligned crystals like diamond thus facilitate better movement of heat.

In graphite C—C bond acquire some double bond character, hence, higher bond order than in diamond.

## 13. Group 15

### [VA-The Nitrogen Family]

1. The order of the oxidation state of the phosphorus atom in  $\text{H}_3\text{PO}_2$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{PO}_3$  and  $\text{H}_4\text{P}_2\text{O}_6$  is

[JEE Advanced 2017, Only One Correct Option]

(a)  $\text{H}_3\text{PO}_4 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6$   
 (b)  $\text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2$   
 (c)  $\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_4$   
 (d)  $\text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6$

Ans. (b)  $\text{H}_3\overset{+5}{\text{P}}\text{O}_4 > \text{H}_4\overset{+4}{\text{P}}_2\text{O}_6 > \text{H}_3\overset{+3}{\text{P}}\text{O}_3 > \text{H}_3\overset{+1}{\text{P}}\text{O}_2$

### Paragraph (Q. Nos. 2-3)

Upon heating  $\text{KClO}_3$  in presence of catalytic amount of  $\text{MnO}_2$ , a gas W is formed. Excess amount of W reacts with white phosphorus to give X. The reaction of X with pure  $\text{HNO}_3$  gives Y and Z.

2. Y and Z are, respectively

(a)  $\text{N}_2\text{O}_4$  and  $\text{HPO}_3$  (b)  $\text{N}_2\text{O}_4$  and  $\text{H}_3\text{PO}_3$   
 (c)  $\text{N}_2\text{O}_3$  and  $\text{H}_3\text{PO}_4$  (d)  $\text{N}_2\text{O}_5$  and  $\text{HPO}_3$

Ans. (d)

3. W and X are, respectively

(a)  $\text{O}_2$  and  $\text{P}_4\text{O}_{10}$  (b)  $\text{O}_2$  and  $\text{P}_4\text{O}_6$   
 (c)  $\text{O}_3$  and  $\text{P}_4\text{O}_6$  (d)  $\text{O}_3$  and  $\text{P}_4\text{O}_{10}$

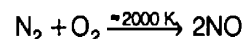
Ans. (a)

4. Assertion (A) Nitrogen and oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen.

Reason (R) The reaction between nitrogen and oxygen requires high temperature. [JEE Main 2015]

(a) Both Assertion and Reason are correct and the reason is the correct explanation for the Assertion  
 (b) Both Assertion and Reason are correct but the reason is not the correct explanation for the Assertion  
 (c) The Assertion is incorrect but the Reason is correct  
 (d) Both the Assertion and Reason are incorrect

Ans. (a) Nitrogen is an inert gas because of the presence of strong bond. That's why although there is 78%  $\text{N}_2$  in the atmosphere but nitrogen oxide is not formed under ordinary conditions. But when temperature is high enough i.e.  $\approx 2000\text{ K}$ , it reacts with oxygen to form nitrogen oxide.



Thus, Assertion and Reason are true and Reason is the correct explanation of the Assertion.

5. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen?

[JEE Advanced 2012, Single Option]

(a)  $\text{HNO}_3$ ,  $\text{NO}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{N}_2$   
 (b)  $\text{HNO}_3$ ,  $\text{NO}$ ,  $\text{N}_2$ ,  $\text{NH}_4\text{Cl}$   
 (c)  $\text{HNO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NO}$ ,  $\text{N}_2$   
 (d)  $\text{NO}$ ,  $\text{HNO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{N}_2$

Ans. (b) Let oxidation number of "N" be x.

$$\text{In } \text{HNO}_3, +1 + x + 3(-2) = 0$$

$$\Rightarrow x = +5$$

$$\text{In } \text{NO}, x - 2 = 0$$

$$\Rightarrow x = +2$$

$$\text{In } \text{N}_2, x = 0$$

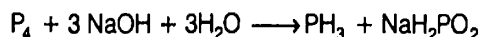
$$\text{In } \text{NH}_4\text{Cl}, x + 4 - 1 = 0$$

$$\Rightarrow x = -3$$

6. The reaction of white phosphorus with aqueous  $\text{NaOH}$  gives phosphine along with another phosphorus containing compound. The reaction type, the oxidation states of phosphorus in phosphine and the other product respectively are [JEE Advanced 2012, Single Option]

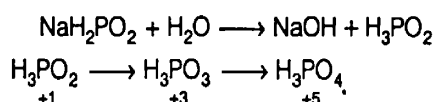
- (a) redox reaction; - 3 and - 5  
 (b) redox reaction; 3 and + 5  
 (c) disproportionation reaction; - 3 and + 5  
 (d) disproportionation reaction; - 3 and + 3

**Ans. (c)** The reaction of white phosphorus with aqueous alkali is



In the above reaction phosphorus is simultaneously oxidized [ $P_4(0) \longrightarrow NaH_2\overset{+1}{P}O_2$ ] as well as reduced [ $P_4(0) \longrightarrow \overset{-3}{P}H_3$ ].

Therefore, this is an example of disproportionation reaction. Oxidation number of phosphorus in  $PH_3$  is - 3 and in  $NaH_2PO_2$  is + 1. However, + 1 oxidation no. is not given in any option, one might think that  $NaH_2PO_2$  has gone to further decomposition on heating.



**7. Extra pure  $N_2$  can be obtained by heating**

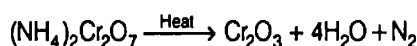
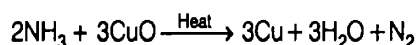
[IIT JEE 2011, Single Option]

- (a)  $NH_3$  with  $CuO$  (b)  $NH_4NO_3$   
 (c)  $(NH_4)_2Cr_2O_7$  (d)  $Ba(N_3)_2$

**Ans. (d)**  $Ba(N_3)_2 \xrightarrow{\text{Heat}} Ba(s) + 3N_2(g)$

Azide salt of barium can be obtained in purest form as well as the decomposition product contain solid Ba as byproduct along with gaseous nitrogen, hence no additional step of separation is required.

Other reactions are :  $NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2H_2O$



**8. Which of the following properties is not shown by  $NO$ ?**

[JEE Main 2014]

- (a) it is diamagnetic in gaseous state  
 (b) it is a neutral oxide  
 (c) it combines with oxygen to form nitrogen dioxide  
 (d) its bond order is 2.5

**Ans. (a)**  $NO$  is paramagnetic in gaseous state because in gaseous state, it has one unpaired electron.

Total number of electron present =  $7 + 8 = 15e^-$

Hence, there must be the presence of unpaired electron in gaseous state while in liquid state, it dimerises due to unpaired electron.

**9. Which of the following is the wrong statement?**

- (a)  $ONCl$  and  $ONO^-$  are not isoelectronic [JEE Main 2013]  
 (b)  $O_3$  molecule is bent  
 (c) ozone is violet black in solid state  
 (d) ozone is diamagnetic gas

**Ans. (a)** (a)  $ONCl = 8 + 7 + 17 = 32$  electrons

$ONO^- = 8 + 7 + 8 + 1 = 24$  electrons (correct)

- (b)   $O$  central atom  $O$  is  $sp^2$  hybridised with one lone pair, so bent shape. (correct)

- (c) In solid state, ozone is violet black (correct)  
 (d)  $O_3$  has no unpaired electrons, so diamagnetic. (correct)  
 Hence, no option is wrong.

**10. The molecule having smaller bond angle is [AIEEE 2012]**

- (a)  $NCl_3$  (b)  $AsCl_3$  (c)  $SbCl_3$  (d)  $PCl_3$

**Ans. (c)**

|                                                                  |                                                                                                  |
|------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|
| $\begin{array}{c} N \\   \\ P \\   \\ As \\   \\ Sb \end{array}$ | $\left. \begin{array}{l} \text{Group} = 15 \\ \text{Valence electrons} \end{array} \right\} = 5$ |
|------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|

$MCl_3$  has  $sp^3$ -hybridised  $M$  - elements with one lone pair. Lone pair and bond pair repulsion decreases bond angle.

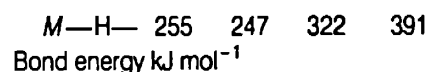
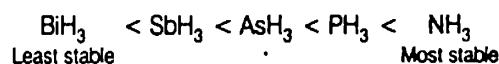
However, the bond pair electrons are much farther away from the central atom than they are in  $PCl_3$ ,  $AsCl_3$  and  $SbCl_3$ . Thus, bond angle decreases from  $NCl_3$  (maximum) to  $SbCl_3$  (minimum).

**11. Which of the following Statements is wrong?**

[AIEEE 2011]

- (a) The stability of hydrides increases from  $NH_3$  to  $BiH_3$  in group 15 of the periodic table  
 (b) Nitrogen can't form  $d\pi-p\pi$  bond.  
 (c) Single  $N-N$  bond is weaker than the single  $P-P$  bond  
 (d)  $N_2O_4$  has two resonance structures

**Ans. (a)** (a) Thermal stability of the hydrides decreases as we go down the group in periodic table of group 15 (N-family)



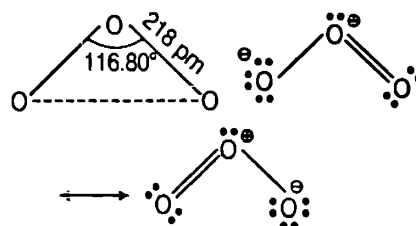
## 14. Group 16 [VI-A Oxygen family]

**1. The correct statement(s) about  $O_3$  is (are)**

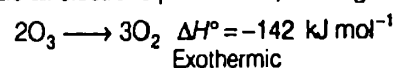
[JEE Advanced 2013, More than One Option]

- (a)  $O-O$  bond lengths are equal  
 (b) thermal decomposition of  $O_3$  is endothermic  
 (c)  $O_3$  is diamagnetic in nature  
 (d)  $O_3$  has a bent structure

**Ans. (a, c, d)** Process is endothermic if it takes place with absorption of heat.



bent molecule all electrons paired thus, diamagnetic



Thus, (b) is incorrect. (a, c, d) are correct.

**2. Which of the following statements regarding sulphur is incorrect? [AIEEE 2011]**

- (a)  $S_2$  molecule is paramagnetic.  
 (b) the vapour at  $200^\circ\text{C}$  consists mostly of  $S_8$  rings.



- (c) at 600°C, the gas mainly consists of  $S_2$  molecules.  
 (d) the oxidation state of sulphur is never less than + 4 in its compounds.

**Ans. (d)**

- (a)  $S_2$  molecule is paramagnetic due to the presence of unpaired electron in MO and is blue-coloured compound—thus true.  
 (b) The vapour at 200°C consists mostly of  $S_8$  rings, thus correct.  
 (c) At 600°C, the gas mainly consists of  $S_2$  molecules—thus correct.  
 (d) Oxidation states of sulphur are

|     |    |               |
|-----|----|---------------|
| - 2 | in | $H_2S$        |
| 0   | in | $S_8$         |
| + 2 | in | $S_2O_3^{2-}$ |
| + 4 | in | $SO_2$        |
| + 6 | in | $SO_3$        |

Thus, incorrect. (Valency can be less than 4).

**3. Identify the incorrect statement from the following.**

[AIEEE 2011]

- (a) Oxides of nitrogen in the atmosphere can cause the depletion of ozone layer  
 (b) Ozone absorbs the intense ultraviolet radiations of the sun  
 (c) Depletion of ozone layer is because of its chemical reactions with chlorofluorocarbons  
 (d) Ozone absorbs infrared radiations

**Ans. (d)** For healthy aquatic life, amount of dissolved oxygen should be 10 ppm.

## 15. Group 17

### [VIIA-The Halogen Family]

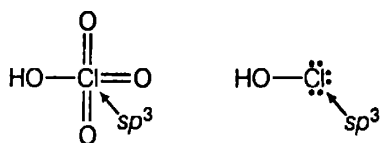
**1. The correct statement(s) about the oxoacids,  $HClO_4$  and  $HClO$ , is (are)**

[JEE Advanced 2017, One or More Than One Correct Option]

- (a) The central atom in both  $HClO_4$  and  $HClO$  is  $sp^3$ -hybridised  
 (b)  $HClO_4$  is formed in the reaction between  $Cl_2$  and  $H_2O$   
 (c) The conjugate base of  $HClO_4$  is weaker base than  $H_2O$   
 (d)  $HClO_4$  is more acidic than  $HClO$  because of the resonance stabilisation of its anion

**Ans. (a, c, d)**

(a)



- (b) Incorrect :  $Cl_2 + H_2O \longrightarrow HCl + HOCl$   
 (c)  $HClO_4$  is stronger acid than  $H_2O$ .  
 (d)  $ClO_4^-$  is more stable than  $ClO^-$ .

**2. The colour of the  $X_2$  molecules of group 17 elements changes gradually from yellow to violet down the group. This is due to**

[JEE Advanced 2017, One or More Than One Correct Option]

- (a) decrease in  $\pi^* - \sigma^*$  gap down the group  
 (b) decrease in ionisation energy down the group  
 (c) the physical state of  $X_2$  at room temperature changes from gas to solid down the group  
 (d) decreases in HOMO-LUMO gap down the group

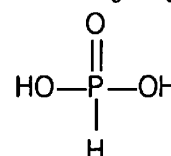
**Ans. (a,d)** Colour of halogen arises due to transition from HOMO to LUMO in the visible region. On moving down a group, the difference in energy between HOMO and LUMO decreases electronic transition occur more easily and colour intensity increases.

**3. The pair in which phosphorus atoms have a formal oxidation state of +3 is**

[JEE Main 2016]

- (a) pyrophosphorous and hypophosphoric acids  
 (b) orthophosphorous and hypophosphoric acids  
 (c) pyrophosphorous and pyrophosphoric acids  
 (d) orthophosphorous and pyrophosphorous acids

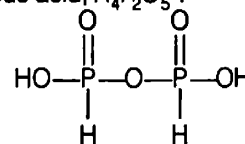
**Ans. (d)** Orthophosphorous acid,  $H_3PO_3$  :



$$H \overset{x}{P} O \quad 3 + x + 3(-2) = 0$$

or  $x = +3$

Pyrophosphorous acid,  $H_4P_2O_5$  :



$$H_4 \overset{x}{P}_2 O_5 = 4 + 2x + 5(-2) = 0$$

$$4 + 2x - 10 = 0$$

$$x = +3$$

**4. Which among the following is the most reactive?**

[JEE Main 2015]

- (a)  $Cl_2$  (b)  $Br_2$  (c)  $I_2$  (d)  $ICl$

**Ans. (d)**  $Cl_2$ ,  $Br_2$  and  $I_2$  are homonuclear diatomic molecule in which electronegativity of the combining atoms is same, so they are more stable and less reactive, whereas,  $I$  and  $Cl$  have different electronegativities and bond between them are polarised and hence, reactive. Therefore, interhalogen compounds are more reactive.

**Time Saving Technique** In this type of question of halogen, only go through the polarity of the molecule. As we know, diatomic molecule does not have polarity but molecules with dissimilar sizes have polarity resulting in more reactivity.

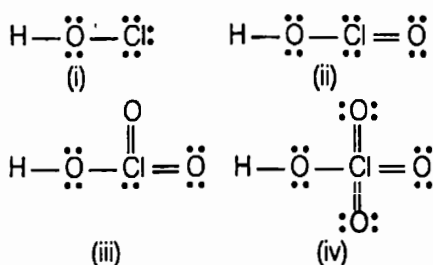
**5. The correct statement(s) regarding,**

[JEE Advanced 2015]

- (i)  $HClO$ ,  
 (ii)  $HClO_2$ ,  
 (iii)  $HClO_3$  and  
 (iv)  $HClO_4$  is (are)

- (a) the number of  $Cl=O$  bonds in (ii) and (iii) together is two  
 (b) the number of lone pair of electrons on  $Cl$  in (ii) and (iv) together is three  
 (c) the hybridisation of  $Cl$  in (iv) is  $sp^3$   
 (d) amongst (i) to (iv), the strongest acid is (i)

Ans. (a)

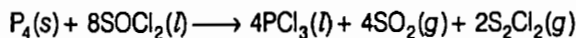


- (a) Number of  $\text{Cl}^- - \text{O}$  bonds in (ii) and (iii) together is three. Hence, wrong.  
 (b) Number of lone pair on Cl in (ii) and (iii) together is three. Hence, correct.  
 (c) In (iv), Cl is  $\text{sp}^3$ -hybridised. Hence, correct.  
 (d) Amongst (i) to (iv), the strongest acid is (iv). Hence, wrong.

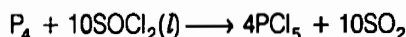
6. The product formed in the reaction of  $\text{SOCl}_2$  with white phosphorus is [JEE Advanced 2014, Single Option]

- (a)  $\text{PCl}_3$  (b)  $\text{SO}_2\text{Cl}_2$   
 (c)  $\text{SCl}_2$  (d)  $\text{POCl}_3$

Ans. (a) White phosphorus on reaction with thionyl chloride ( $\text{SOCl}_2$ ) produces phosphorus trichloride.



But if amount of thionyl chloride ( $\text{SOCl}_2$ ) is in excess then it produces phosphorus pentachloride.



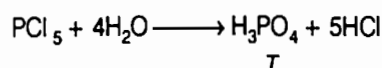
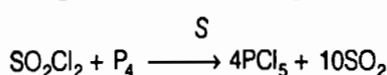
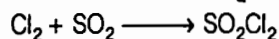
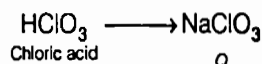
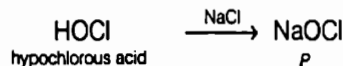
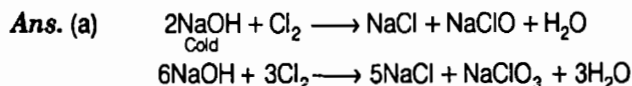
Hence, (a) is the correct choice.

7. The reactions of  $\text{Cl}_2$  gas with cold-dilute and hot-concentrated  $\text{NaOH}$  in water give sodium salts of two (different) oxoacids of chlorine, P and Q, respectively. The  $\text{Cl}_2$  gas reacts with  $\text{SO}_2$  gas, in the presence of charcoal, to give a product R. R reacts with white phosphorus to give a compound S. On hydrolysis, S gives an oxoacid of phosphorous T.

[JEE Advanced 2013, Passage Based]

P and Q respectively, are the sodium salts of

- (a) hypochlorous and chloric acids  
 (b) hypochlorous and chlorous acids  
 (c) chloric and perchloric acids  
 (d) chloric and hypochlorous acids

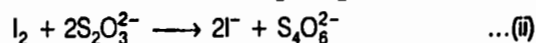
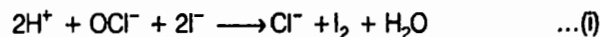


8. Bleaching powder and bleach solution are produced on a large scale and used in several house hold products. The effectiveness of bleach solution is often measured by iodometry. 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N  $\text{Na}_2\text{S}_2\text{O}_3$  was used to reach the end point. The molarity of the household bleach solution, is

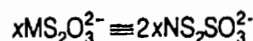
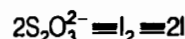
[JEE Advanced 2012, Passage Based]

- (a) 0.48 M (b) 0.96 M  
 (c) 0.24 M (d) 0.024 M

Ans. (c) The involved redox reactions are



$$\therefore \text{I} = \frac{\text{OCl}^-}{2}$$



25 mL of bleach solution = 48 mL of 0.25 N  $\text{S}_2\text{O}_3^{2-}$  Solution

$$\therefore 25 \times N_1(\text{bleach}) = 48 \times 0.25$$

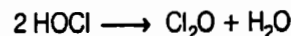
$$\therefore N_1 = 0.48 \text{ N}$$

$$\therefore M(\text{bleach}) = \frac{0.48}{2} = 0.24 \text{ M}$$

9. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid, is

- (a)  $\text{Cl}_2\text{O}$  (b)  $\text{Cl}_2\text{O}_7$   
 (c)  $\text{ClO}_2$  (d)  $\text{Cl}_2\text{O}_8$

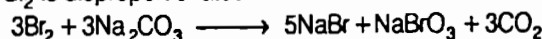
Ans. (a) Bleaching powder is  $\text{Ca}(\text{OCl})\text{Cl}$ . Therefore, the oxoacid whose salt is present in bleaching powder is  $\text{HOCl}$ . Anhydride of  $\text{HOCl}$  is  $-\text{Cl}_2\text{O}$  as



10. Reaction of  $\text{Br}_2$  with  $\text{Na}_2\text{CO}_3$  in aqueous solution gives sodium bromide and sodium bromate with evolution of  $\text{CO}_2$  gas. The number of sodium bromide molecules involved in the balanced chemical equation is

[IIT JEE 2011, Integer Type]

Ans. (5)  $\text{Br}_2$  is disproportionated in basic medium as



11. Among the following, the number of compounds that can react with  $\text{PCl}_5$  to give  $\text{POCl}_3$  is  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{P}_4\text{O}_{10}$ .

[IIT JEE 2011, Integer Type]

- (a) 1 (b) 2  
 (c) 3 (d) 4

Ans. (a)  $\text{PCl}_5$  produces  $\text{POCl}_3$  with the following reagents.

## 16. The Transition and Inner Transition Elements

1. The colour of  $\text{KMnO}_4$  is due to [JEE Main 2015]  
 (a)  $M \rightarrow L$  charge transfer transition  
 (b)  $d-d$  transition  
 (c)  $L \rightarrow M$  charge transfer transition  
 (d)  $\sigma-\delta$  transition

**Ans. (c)**  $\text{KMnO}_4 \longrightarrow \text{K}^+ + \text{MnO}_4^-$   
 $\therefore$  In  $\text{MnO}_4^-$ , Mn has +7 oxidation state having no electron in  $d$ -orbitals.

It is considered that higher the oxidation state of metal, greater is the tendency to occur  $L \rightarrow M$  charge transfer, because ligand is able to donate the electrons into the vacant  $d$ -orbital of metal. Since, charge transfer is Laporte as well as spin allowed, therefore, it shows colour.

**Time Saving Technique** There is no need to check all the four options. Just find out the oxidation state of metal ion. If oxidation state is highest and ligand present there is of electron donating nature, gives LMCT, which shows more intense colour.

2. The correct statement(s) about  $\text{Cr}^{2+}$  and  $\text{Mn}^{3+}$  is/are [atomic number of Cr = 24 and Mn = 25]

[JEE Advanced 2015, More than One Option]

- (a)  $\text{Cr}^{2+}$  is a reducing agent  
 (b)  $\text{Mn}^{3+}$  is an oxidising agent  
 (c) both  $\text{Cr}^{2+}$  and  $\text{Mn}^{3+}$  exhibit  $d^4$  electronic configuration  
 (d) when  $\text{Cr}^{2+}$  is used as a reducing agent, the chromium ion attains  $d^5$  electronic configuration

**Ans. (a, b, c)** (a) In aqueous solution  $\text{Cr}^{2+}$  ( $3d^4$ ) acts as a reducing agent, oxidising itself to  $\text{Cr}^{3+}$  ( $3d^3$ ) that gives a completely half-filled  $t_{2g}$  level in octahedral ligand field of  $\text{H}_2\text{O}$ .

(b)  $\text{Mn}^{3+}$  ( $3d^4$ ) is an oxidising agent as it is reduced to  $\text{Mn}^{2+}$  ( $3d^5$ ), a completely half-filled stable configuration.

(c) Both  $\text{Cr}^{2+}$  and  $\text{Mn}^{3+}$  have  $d^4$  configuration.

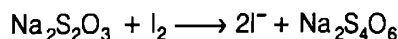
(d)  $3d^4 \text{Cr}^{2+}(\text{aq}) \xrightarrow{\text{RA}} \text{Cr}^{3+}(\text{aq}) + e^-$

Hence (d) is wrong statement.

3. Consider the following list of reagents, acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ , alkaline  $\text{KMnO}_4$ ,  $\text{CuSO}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{O}_3$ ,  $\text{FeCl}_3$ ,  $\text{HNO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_3$ . The total number of reagents that can oxidise aqueous iodide to iodine is

[JEE Advanced 2014, Integer Type]

**Ans. (7)** Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{CuSO}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{O}_3$ ,  $\text{FeCl}_3$  and  $\text{HNO}_3$  oxidise aq. iodide to iodine. Alkaline  $\text{KMnO}_4$  oxidise aq. iodide to  $\text{IO}_3^-$ .  $\text{Na}_2\text{S}_2\text{O}_3$  is a strong reducing agent which on reaction with  $\text{I}_2$  produces  $\text{I}^-$ .



Therefore, no reaction takes place between  $\text{Na}_2\text{S}_2\text{O}_3$  and iodide ion. Hence, correct integer is (7).

4. The colour of light absorbed by an aqueous solution of  $\text{CuSO}_4$  is [JEE Advanced 2012, Single Option]

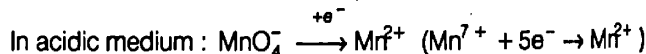
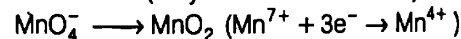
- (a) orange-red (b) blue-green  
 (c) yellow (d) violet

**Ans. (a)** The aqueous solution of  $\text{CuSO}_4$  consist of the complex  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  ion which absorbed in orange-red region and impart deep blue colouration to solution.

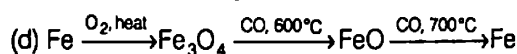
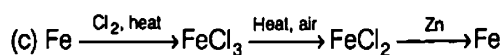
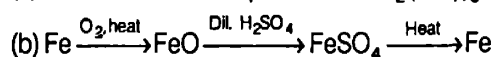
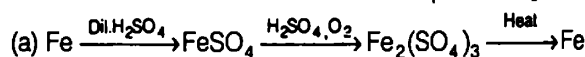
5. Reduction of the metal centre in aqueous permanganate ion involves [IIT JEE 2011, More than One Option]

- (a) three electrons in neutral medium  
 (b) five electrons in neutral medium  
 (c) three electrons in alkaline medium  
 (d) five electrons in acidic medium

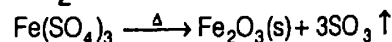
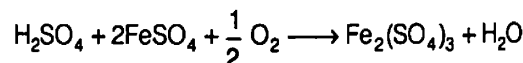
**Ans. (a, d)** In neutral medium : (Very dilute alkali solution)



6. Which series of reactions correctly represents chemical relations related to iron and its compound? [JEE Main 2014]

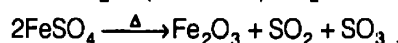
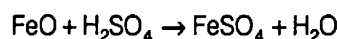


**Ans. (d)** (a)  $\text{Fe} + \text{dil. H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{H}_2$

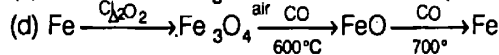


The given reaction is incorrect in question.

(b)  $\text{Fe} \xrightarrow{\text{O}_2} \text{FeO}$  (It could also be  $\text{Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$ )



(c)  $\text{Fe} \xrightarrow{\Delta} \text{FeCl}_3 \xrightarrow{\Delta} \text{No reaction}$ , (It can not give  $\text{FeCl}_2$ )



This is the correct equation.

7. Which of the following arrangements does not represent the correct order of the property stated against it?

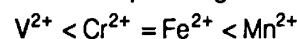
[JEE Main 2013]

- (a)  $\text{V}^{2+} < \text{Cr}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+}$  Paramagnetic behaviour  
 (b)  $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+}$  ionic size  
 (c)  $\text{Co}^{3+} < \text{Fe}^{3+} < \text{Cr}^{3+} < \text{Sc}^{3+}$  stability in aqueous solution  
 (d)  $\text{Sc} < \text{Ti} < \text{Cr} < \text{Mn}$  number of oxidation states

**Ans. (d)** (a)  $\text{V}^{2+} = 3$  unpaired  $e^-$ ,  $\text{Cr}^{2+} = 4$  unpaired  $e^-$



Hence, the order of paramagnetic behaviour should be



(b) Ionic size decreases from left to right in the same period.

(c)  $\text{Co}^{3+} / \text{Co}^{2+} = 1.97$ ;  $\text{Fe}^{3+} / \text{Fe}^{2+} = 0.77$

$\text{Cr}^{3+} / \text{Cr}^{2+} = -0.41$   $\text{Sc}^{3+}$  is highly stable because it does not show +2 oxidation state.

(d) The oxidation states increase as we go from group 3 to group 7 in the same period.

8. Four successive members of the first row transition elements listed below with atomic numbers. Which one of them is expected to have the highest  $E^{\circ}_{M^{3+}/M^{2+}}$  value?

(a) Cr(Z = 24) (b) Mn(Z = 25) [JEE Main 2013]  
(c) Fe(Z = 26) (d) Co(Z = 27)

Ans. (d) Standard reduction potential (SRP) value normally increases from left to right in the period of d-block elements. Some SRP value are exceptionally higher due to stability of product ion. e.g.,

$$E^{\circ}(\text{Mn}^{3+}/\text{Mn}^{2+}) = +1.57 \text{ V}; E^{\circ}(\text{Co}^{3+}/\text{Co}^{2+}) = +1.97 \text{ V}$$

Thus,  $E^{\circ}(M^{3+}/M^{2+})$  is highest for Co.

9. Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is incorrect? [AIEEE 2012]

(a) Ferrous oxide is more basic in nature than the ferric oxide  
(b) Ferrous compounds are relatively more ionic than the corresponding ferric compounds  
(c) Ferrous compounds are less volatile than the corresponding ferric compounds  
(d) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds

Ans. (d) (a)  $\text{FeO} > \text{Fe}_2\text{O}_3$  (basic) correct.

(b)  $\text{FeCl}_2 > \text{FeCl}_3$  (ionic), larger the charge, greater the polarising power thus, greater the covalent nature. Thus, correct.

(c)  $\text{Fe}^{2+}$  salts are more ionic thus, less volatile than  $\text{Fe}^{3+}$  salts. Thus, correct.

(d) Greater the covalent nature, more easily they are hydrolysed. Thus,  $\text{FeCl}_3$  is more hydrolysed than  $\text{FeCl}_2$ . Thus, statement (d) is incorrect.

## 17. Metallurgical Extraction

1. Which one of the following ores is best concentrated by froth floatation method? [JEE Main 2016]

(a) Siderite  
(b) Galena  
(c) Malachite  
(d) Magnetite

Ans. (b) Sulphide ores are concentrated by froth floatation method e.g. Galena ( $\text{PbS}$ )

2. Galvanisation is applying a coating of [JEE Main 2016]

(a) Cr (b) Cu  
(c) Zn (d) Pb

Ans. (c) Zinc metal is the most stable metal to cover iron surfaces. The process of coating the iron surface by zinc is called galvanisation.

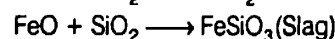
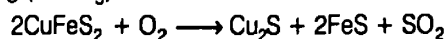
3. Extraction of copper from copper pyrite ( $\text{CuFeS}_2$ ) involves [JEE Advanced 2016, One or More Than One Option Correct]

(a) crushing followed by concentration of the ore by froth-floatation  
(b) removal of iron as slag  
(c) self reduction step to produce 'blister copper' following evolution of  $\text{SO}_2$   
(d) refining of 'blister copper' by carbon reduction

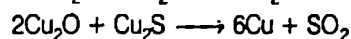
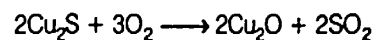
Ans. (a,b,c)  $\text{CuFeS}_2$  (copper pyrite) is converted into copper into following steps:

Step I Crushing (grinding) followed by concentration by froth-floatation process.

Step II Roasting of ore in the presence of  $\text{SiO}_2$  which removes iron as slag ( $\text{FeSiO}_3$ ).



Step III Self-reduction in Bessemer converter



Copper obtained is blister copper (98% pure).

Step IV Refining of blister copper is done by electrolysis

Impure copper — Anode

Pure copper — Cathode

At anode :  $\text{Cu} \longrightarrow \text{Cu}^{2+} + 2e^-$

At cathode :  $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$

Carbon-reduction method is not used. Thus, (d) is incorrect.

4. In the context of the Hall-Heroult process for the extraction of Al, which of the following statements is false? [JEE Main 2015]

(a) CO and  $\text{CO}_2$  are produced in this process  
(b)  $\text{Al}_2\text{O}_3$  is mixed with  $\text{CaF}_2$  which lowers the melting point of the mixture and brings conductivity  
(c)  $\text{Al}^{3+}$  is reduced at the cathode to form Al  
(d)  $\text{Na}_3\text{AlF}_6$  serves as the electrolyte

Ans. (d) (a) In Hall-Heroult process for extraction of Al, carbon anode is oxidised to CO and  $\text{CO}_2$ .

(b) When  $\text{Al}_2\text{O}_3$  is mixed with  $\text{CaF}_2$ , it lowers the melting point of the mixture and brings conductivity.

(c)  $\text{Al}^{3+}$  is reduced at cathode to form Al.

(d) Here,  $\text{Al}_2\text{O}_3$  is an electrolyte, undergoing the redox process.  $\text{Na}_3\text{AlF}_6$  although is an electrolyte but serves as a solvent, not electrolyte.

5. Match the anionic species given in Column I that are present in the ore (s) given in Column II.

|    | Column I  | Column II    |
|----|-----------|--------------|
| A. | Carbonate | P. Siderite  |
| B. | Sulphide  | Q. Malachite |
| C. | Hydroxide | R. Bauxite   |
| D. | Oxide     | S. Calamine  |
|    |           | T. Argentite |

[JEE Advanced 2015, Matching Type]

Ans. (d) Siderite =  $\text{FeCO}_3$ , Malachite =  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$   
Bauxite =  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  consisting some  $\text{Al}(\text{OH})_3$   
Calamine =  $\text{ZnCO}_3$ , Argentite =  $\text{Ag}_2\text{S}$

6. Copper is purified by electrolytic refining of blister copper. The correct statement(s) about this process is/are [JEE Advanced 2015, Single Option]

(a) impure Cu strip is used as cathode  
(b) acidified aqueous  $\text{CuSO}_4$  is used as electrolyte  
(c) pure Cu deposits at cathode  
(d) impurities settle as anode-mud

**Ans. (d)**

(a) is wrong statement. Impure copper is set as anode where copper is oxidised to  $\text{Cu}^{2+}$  and goes into electrolytic solutions.

(b)  $\text{CuSO}_4$  is used as an electrolyte in purification process.

(c) Pure copper is deposited at cathode as:

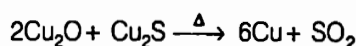


(d) Less active metals like Ag, Au etc., settle down as anode mud.

**7.** Upon heating with  $\text{Cu}_2\text{S}$ , the reagent(s) that give copper metal is/are [JEE Advanced 2014, More than One Option]

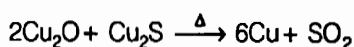
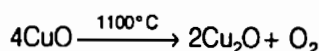
- (a)  $\text{CuFeS}_2$  (b)  $\text{CuO}$   
(c)  $\text{Cu}_2\text{O}$  (d)  $\text{CuSO}_4$

**Ans. (b, c, d)** (b)  $4\text{CuO} \xrightarrow{1100^\circ\text{C}} 2\text{Cu}_2\text{O} + \text{O}_2$

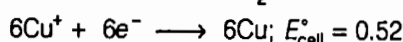
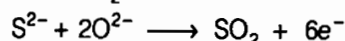
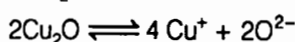
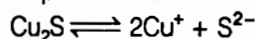


(c)  $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \xrightarrow{\Delta} 6\text{Cu} + \text{SO}_2$

(d)  $\text{CuSO}_4 \xrightarrow{720^\circ\text{C}} \text{CuO} + \text{SO}_2 + \frac{1}{2}\text{O}_2$



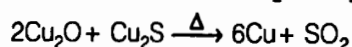
Reaction is believed to proceed as



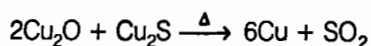
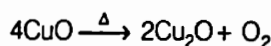
Here, copper sulphide is reduced to copper metal. Solidified copper has blistered appearance due to evolution of  $\text{SO}_2$  and thus obtained copper is known as blister copper.

Other compounds which give Cu are

(i)  $\text{CuO}$  as  $4\text{CuO} \xrightarrow{1100^\circ\text{C}} 2\text{Cu}_2\text{O} + \text{O}_2$



(ii)  $\text{CuSO}_4$  as  $\text{CuSO}_4 \xrightarrow{720^\circ\text{C}} \text{CuO} + \text{SO}_2 + \frac{1}{2}\text{O}_2$



While  $\text{CuFeS}_2$  will not give Cu on heating. The heating in the presence of  $\text{O}_2$  gives  $\text{Cu}_2\text{S}$  and  $\text{FeS}$  with the evolution of  $\text{SO}_2$ .

**8.** Sulphide ores are common for the metals

[JEE Advanced 2013, Single Option]

- (a) Ag, Cu and Pb (b) Ag, Cu and Sn  
(c) Ag, Mg and Pb (d) Al, Cu and Pb

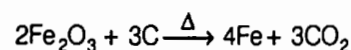
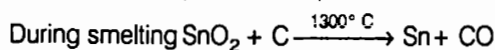
**Ans. (a)**

| Element | Ores                                              | Name           |
|---------|---------------------------------------------------|----------------|
| Ag      | $\text{Ag}_2\text{S}$                             | Argentite      |
| Cu      | $\text{CuFeS}_2$                                  | Copper pyrites |
| Pb      | $\text{PbS}$                                      | Galena         |
| Sn      | $\text{SnO}_2$                                    | Cassiterite    |
| Mg      | $\text{MgCO}_3 \cdot \text{CaCO}_3$               | Dolomite       |
| Al      | $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ | Bauxite        |

**9.** The carbon-based reduction method is not used for the extraction of [JEE Advanced 2013, More than One Option]

- (a) tin from  $\text{SnO}_2$   
(b) iron from  $\text{Fe}_2\text{O}_3$   
(c) aluminium from  $\text{Al}_2\text{O}_3$   
(d) magnesium from  $\text{MgCO}_3, \text{CaCO}_3$

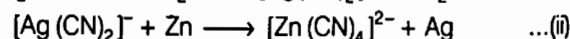
**Ans. (c, d)** Al has greater affinity for oxygen hence oxide is not reduced by carbon.  $\text{MgO}$  and  $\text{CaO}$  (formed in the calcination from carbonates) are stable species and not reduced by carbon.



**10.** In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agents used are

- (a)  $\text{O}_2$  and  $\text{CO}$  respectively [JEE Advanced 2012, Single Option]  
(b)  $\text{O}_2$  and Zn dust respectively  
(c)  $\text{HNO}_3$  and Zn dust respectively  
(d)  $\text{HNO}_3$  and  $\text{CO}$  respectively

**Ans. (b)** The reactions involved in extraction of silver by cyanide process are



In reaction (i), sulphide is oxidized to  $\text{SO}_2$  by oxygen. In the reaction (ii), silver ion ( $\text{Ag}^+$ ) is reduced to Ag by Zn. Therefore,  $\text{O}_2$  is oxidising agent and Zn is reducing agent.

**11.** Oxidation states of the metal in the minerals haematite and magnetite, respectively, are [IIT JEE 2011, Single Option]

- (a) II, III in haematite and III in magnetite  
(b) II, III in haematite and II in magnetite  
(c) II in haematite and II, III in magnetite  
(d) III in haematite and II, III in magnetite

**Ans. (d)** Haematite is  $\text{Fe}_2\text{O}_3$ , in which oxidation number of iron is III. Magnetite is  $\text{Fe}_3\text{O}_4$  which is infact a mixed oxide ( $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ ), hence, iron is present in both II and III oxidation state.

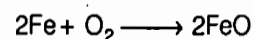
**12.** Extraction of metal from the ore cassiterite involves [IIT JEE 2011, More than One Option]

- (a) carbon reduction of an oxide ore  
(b) self-reduction of a sulphide ore  
(c) removal of copper impurity  
(d) removal of iron impurity

**Ans. (a, d)** The important ore of tin is cassiterite ( $\text{SnO}_2$ ). Tin is extracted from cassiterite ore by carbon reduction method in a blast furnace.



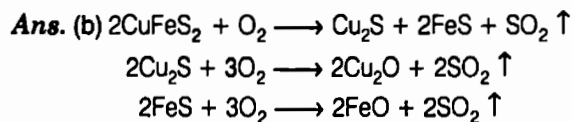
The product often contain traces of iron which is removed by blowing air through the melt to oxidise to  $\text{FeO}$  which then floats to the surface.



**13.** Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcantite ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), atacamite ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ), cuprite ( $\text{Cu}_2\text{O}$ ), copper glance ( $\text{Cu}_2\text{S}$ ) and malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ). However, 80% of the world

copper production comes from the ore chalcopryrite ( $\text{CuFeS}_2$ ). The extraction of copper from chalcopryrite involves partial roasting, removal of iron and self-reduction. [IIT JEE 2010, Passage Based]

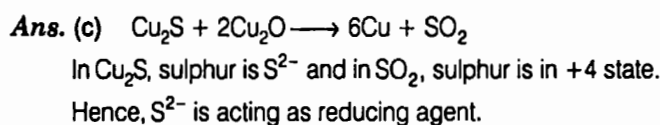
- (i) Partial roasting of chalcopryrite produces  
 (a)  $\text{Cu}_2\text{S}$  and  $\text{FeO}$  (b)  $\text{Cu}_2\text{O}$  and  $\text{FeO}$   
 (c)  $\text{CuS}$  and  $\text{Fe}_2\text{O}_3$  (d)  $\text{Cu}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$



- (ii) Iron is removed from chalcopryrite as  
 (a)  $\text{FeO}$  (b)  $\text{FeS}$   
 (c)  $\text{Fe}_2\text{O}_3$  (d)  $\text{FeSiO}_3$

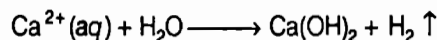


- (iii) In self-reduction, the reducing species is  
 (a)  $\text{S}$  (b)  $\text{O}^{2-}$   
 (c)  $\text{S}^{2-}$  (d)  $\text{SO}_2$

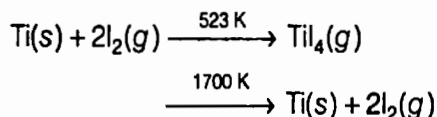


- 14.** The metal that can not be obtained by electrolysis of an aqueous solution of its salts is [JEE Main 2014]  
 (a)  $\text{Ag}$  (b)  $\text{Ca}$   
 (c)  $\text{Cu}$  (d)  $\text{Cr}$

**Ans. (b)** Higher the position of element in the electrochemical series more difficult is the reduction of its cations. If  $\text{Ca}^{2+}(\text{aq})$  is electrolysed, water is reduced in preference to it. Hence, it can not be reduced electrolytically from their aqueous solutions.



- 15.** Which method of purification is represented by the following equation? [AIEEE 2012]



- (a) Zon refining (b) Cupellation  
 (c) Poling (d) van-Arkel

**Ans. (d)** van-Arkel (and de-Boer) process is based on the thermal decomposition of a volatile compound like an iodide, which is first formed by direct combination of metal to be purified and iodine. Metal formed is in purest form. Titanium and zirconium are purified by this method.

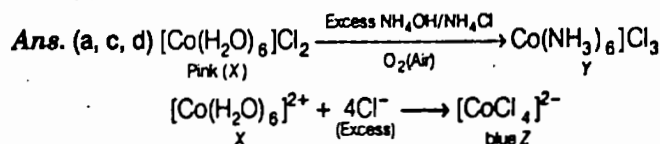
## 18. Coordination Compounds

- 1.** Addition of excess aqueous ammonia to a pink coloured aqueous solution of  $\text{MCl}_2 \cdot 6\text{H}_2\text{O}(\text{X})$  and  $\text{NH}_4\text{Cl}$  gives an octahedral complex Y in the presence of air. In aqueous solution, complex Y behaves as 1 : 3 electrolyte. The reaction of X with excess  $\text{HCl}$  at room temperature results in the formation of a blue coloured complex Z. The

calculated spin only magnetic moment of X and Z is 3.87 B.M., whereas it is zero for complex Y.

Among the following options, which statement(s) is (are) correct? [JEE Advanced 2017, One or More Than Correct Option]

- (a) The hybridisation of the central metal ion in Y is  $d^2sp^3$   
 (b) Addition of silver nitrate to Y gives only two equivalents of silver chloride  
 (c) When X and Y are in equilibrium at  $0^\circ\text{C}$ , the colour of the solution is pink  
 (d) Z is a tetrahedral complex



- (a) Since  $\text{NH}_3$  is moderately strong ligand, hybridisation of cobalt in Y is  $d^2sp^3$ .  
 (b) Cobalt is  $sp^3$ -hybridised in  $[\text{CoCl}_4]^{2-}$ .  
 (c)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 + 3\text{AgNO}_3(\text{aq}) \longrightarrow 3\text{AgCl} \downarrow$   
 (d)  $[\text{CoCl}_4]^{2-} + 6\text{H}_2\text{O} \rightleftharpoons [\text{Co}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^-$ ;  $\Delta H < 0$   
 Blue Pink

- 2.** Which of the following compounds is metallic and ferromagnetic? [JEE Main 2016]

- (a)  $\text{CrO}_2$  (b)  $\text{VO}_2$   
 (c)  $\text{MnO}_2$  (d)  $\text{TiO}_2$

**Ans. (a)** Only three elements iron (Fe), cobalt (Co) and nickel (Ni) show ferromagnetism at room temperature.  $\text{CrO}_2$  is also a metallic and ferromagnetic compound which is used to make magnetic tapes for cassette recorders.

- 3.** The pair having the same magnetic moment is [at. no.  $\text{Cr} = 24$ ,  $\text{Mn} = 25$ ,  $\text{Fe} = 26$  and  $\text{Co} = 27$ ]

[JEE Main 2016]

- (a)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   
 (b)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$   
 (c)  $[\text{CoCl}_4]^{2-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   
 (d)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{CoCl}_4]^{2-}$

**Ans. (a)**

| Complex ion                              | Electronic configuration of metal ion | Number of unpaired electrons (n)                                                      |
|------------------------------------------|---------------------------------------|---------------------------------------------------------------------------------------|
| $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ | $\text{Cr}^{2+}; [\text{Ar}] 3d^4$    | $\boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{\phantom{0}} \boxed{\phantom{0}} : 4$ |
| $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ | $\text{Fe}^{2+}; [\text{Ar}] 3d^6$    | $\boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1} : 4$                     |
| $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ | $\text{Mn}^{2+}; [\text{Ar}] 3d^5$    | $\boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1} : 5$                     |
| $[\text{CoCl}_4]^{2-}$                   | $\text{Co}^{2+}; [\text{Ar}] 3d^7$    | $\boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1} : 3$                     |

- 4.** Among  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{NiCl}_4]^{2-}$ ,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ ,  $\text{Na}_3[\text{CoF}_6]$ ,  $\text{Na}_2\text{O}_2$  and  $\text{CsO}_2$ , the total number of paramagnetic compounds is [JEE Advanced 2016, Single Option Correct]  
 (a) 2 (b) 3  
 (c) 4 (d) 5

Ans. (b)

| Compounds                                               | Hybridisation                  | Unpaired electron(s) | Magnetic character                                           |
|---------------------------------------------------------|--------------------------------|----------------------|--------------------------------------------------------------|
| Ni(CO) <sub>4</sub>                                     | sp <sup>3</sup>                | No                   | Diamagnetic                                                  |
| [NiCl <sub>4</sub> ] <sup>2-</sup>                      | sp <sup>3</sup>                | two                  | Paramagnetic                                                 |
| [Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ] Cl | sp <sup>3</sup> d <sup>2</sup> | No                   | Diamagnetic                                                  |
| Na <sub>3</sub> [CoF <sub>6</sub> ]                     | sp <sup>3</sup> d <sup>2</sup> | three                | Paramagnetic                                                 |
| Na <sub>2</sub> O <sub>2</sub>                          | —                              | No                   | Diamagnetic (O <sub>2</sub> <sup>2-</sup> )                  |
| CsO <sub>2</sub>                                        | —                              | One                  | Paramagnetic                                                 |
|                                                         |                                |                      | O <sub>2</sub> <sup>-</sup> (superoxide ion is paramagnetic) |

5. The geometries of the ammonia complexes of Ni<sup>2+</sup>, Pt<sup>2+</sup> and Zn<sup>2+</sup>, respectively, are

[JEE Advanced 2016, Single Option Correct]

- (a) octahedral, square planar and tetrahedral  
 (b) square planar, octahedral and tetrahedral  
 (c) tetrahedral, square planar and octahedral  
 (d) octahedral, tetrahedral and square planar

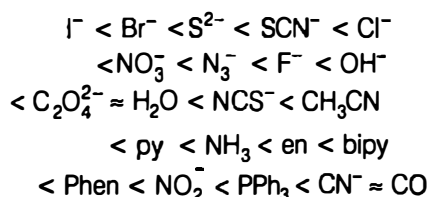
Ans. (a) [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> sp<sup>3</sup>d<sup>2</sup> octahedral[Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> dsp<sup>2</sup> square planar[Zn(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> sp<sup>3</sup> tetrahedral

6. Which of the following compounds is not coloured yellow?

- (a) Zn<sub>2</sub>[Fe(CN)<sub>6</sub>] [JEE Main 2015]  
 (b) K<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>]  
 (c) (NH<sub>4</sub>)<sub>3</sub>[As(Mo<sub>3</sub>O<sub>10</sub>)<sub>4</sub>]  
 (d) BaCrO<sub>4</sub>

Ans. (a) Zn<sub>2</sub>[Fe(CN)<sub>6</sub>], K<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>] and [(NH<sub>4</sub>)<sub>3</sub>As(Mo<sub>3</sub>O<sub>10</sub>)<sub>4</sub>] show colour due to d-d transition while BaCrO<sub>4</sub> is coloured due to charge transfer phenomenon. Further, according to spectrochemical series the strong ligand possessing complex has higher energy and hence lower wavelength. Therefore, complexes containing NO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, O<sup>2-</sup> etc ligands show yellow colour while CN<sup>-</sup> forces the complex to impart white colour.

Spectrochemical series



7. The number of geometric isomers that can exist for square planar [Pt(Cl)(py)(NH<sub>3</sub>)(NH<sub>2</sub>OH)]<sup>+</sup> is (py = pyridine)

[JEE Main 2015]

- (a) 2 (b) 3  
 (c) 4 (d) 6

Ans. (b) [Pt(Cl)(py)(NH<sub>3</sub>)(NH<sub>2</sub>OH)]<sup>+</sup> is square planar complex. The structures are formed by fixing a group and then arranging all the groups.

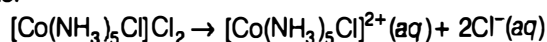
8. If the freezing point of a 0.01 molal aqueous solution of a cobalt (III) chloride-ammonia complex (which behaves as a strong electrolyte) is -0.0558°C, the number of chloride(s) in the coordination sphere of the complex is [K<sub>f</sub> of water = 1.86 K kg mol<sup>-1</sup>] [JEE Advanced 2015, Integer Type]

Ans. (1) + ΔT<sub>f</sub> = iK<sub>f</sub>m

$$\begin{aligned}
 \Delta T_f &= 0 - (-0.0558^\circ\text{C}) \\
 &= 0.0558^\circ\text{C}
 \end{aligned}$$

$$\Rightarrow i \text{ (van't Hoff's factor)} = \frac{0.0558}{1.86 \times 0.01} = 3$$

This indicates that complex upon ionisation produces three ions as:

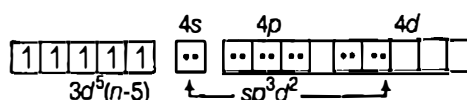
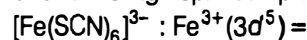


Thus, only one Cl is inside the coordination sphere.

9. For the octahedral complexes of Fe<sup>3+</sup> in SCN<sup>-</sup> (thiocyanato-S) and in CN<sup>-</sup> ligand environments, the difference between the spin only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is [atomic number of Fe = 26]

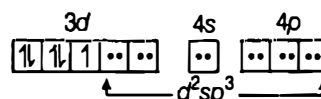
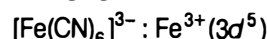
[JEE Advanced 2015, Integer Type]

Ans. (4) When S is donor atom of SCN<sup>-</sup>, it produces weak ligand field and forms high spin complex as



$$\text{Spin only magnetic moment } (\mu_s) = \sqrt{5(5+2)} \text{ BM} = \sqrt{35} \text{ BM}$$

In case of CN<sup>-</sup> ligand, carbon is the donor atom, it produces strong ligand field and forms low spin complex as



$$\text{Spin only magnetic moment } (\mu_s)$$

$$= \sqrt{1(1+2)} \text{ BM}$$

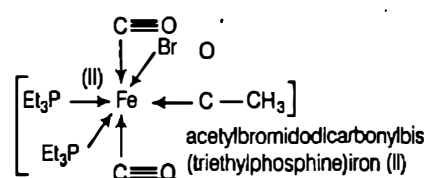
$$= \sqrt{3} \text{ BM}$$

Hence, difference in spin only magnetic moment

$$= \sqrt{35} - \sqrt{3} \approx 4 \text{ BM}$$

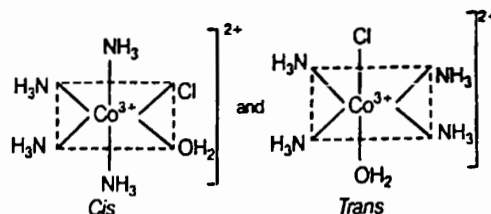
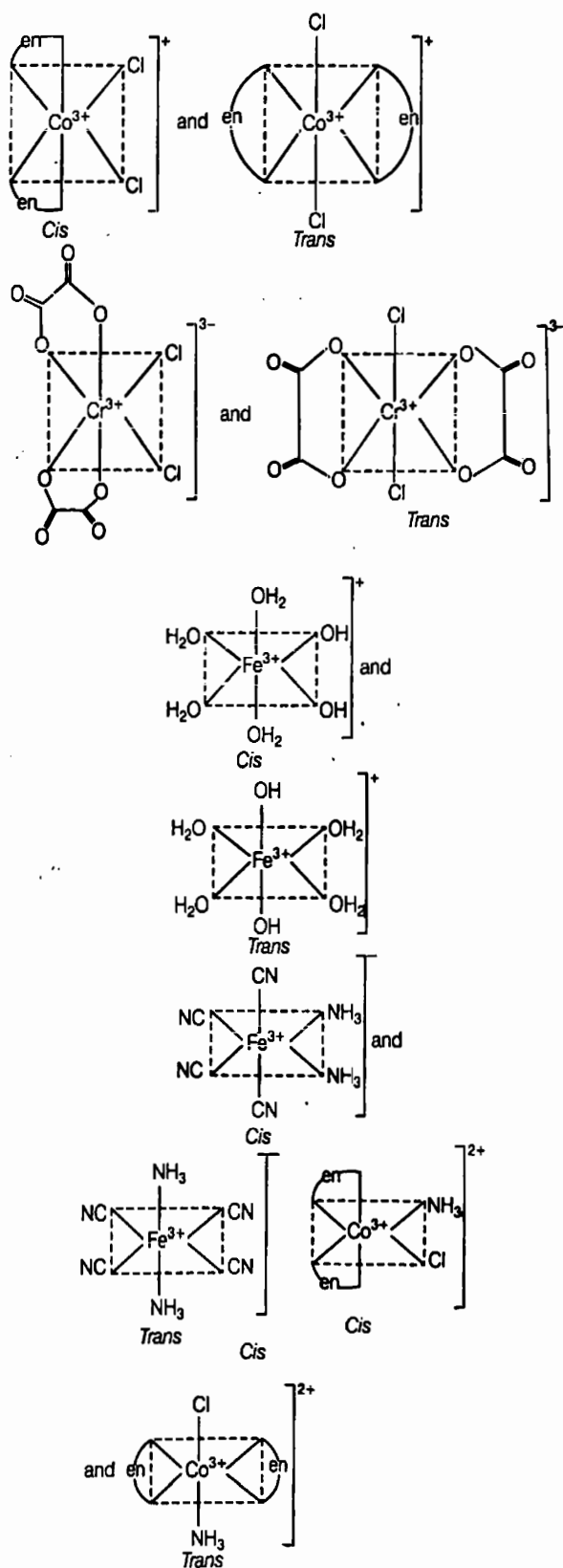
10. In the complex acetyl bromidodicarbonylbis(triethylphosphine) iron (II), the number of Fe—C bond(s) is [JEE Advanced 2015]

Ans. (b)



11. Among the complex ions,  $[\text{Co}(\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2)_2\text{Cl}_2]^+$ ,  $[\text{CrCl}_2(\text{C}_2\text{O}_4)_2]^{3-}$ ,  $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ ,  $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^-$ ,  $[\text{Co}(\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2)_2(\text{NH}_3)\text{Cl}]^{2+}$  and  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$  the number of complex ion(s) that show(s) *cis-trans* isomerism is

[JEE Advanced 2015, Integer Type]

Ans. (6) All six complex will show *cis-trans* isomerism

12. Consider the following complex ions,
- $P$
- ,
- $Q$
- and
- $R$
- .

$$P = [\text{FeF}_6]^{3-}, Q = [\text{V}(\text{H}_2\text{O})_6]^{2+} \text{ and } R = [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$$

The correct order of the complex ions, according to their spin-only magnetic moment values (in BM) is

[JEE Advanced 2013, Single Option]

- (a)  $R < Q < P$  (b)  $Q < R < P$   
(c)  $R < P < Q$  (d)  $Q < P < R$

Ans. (b) In presence of strong ligand (as  $\text{CN}^-$ ,  $\text{CO}$ ,  $\text{NH}_3$ ,  $\text{en}$ ) electrons are paired and electrons from ligands are filled in available inner orbitals

| Complex                                                    | Atomic number of | O.N. | E.C.              | Unpaired electrons | Magnetic moment |
|------------------------------------------------------------|------------------|------|-------------------|--------------------|-----------------|
| $P : [\text{FeF}_6]^{3-}$<br>weak ligand                   | 26               | + 3  | $[\text{Ar}]3d^5$ | 5                  | $\sqrt{35}$ BM  |
| $Q : [\text{V}(\text{H}_2\text{O})_6]^{2+}$<br>weak ligand | 23               | + 2  | $[\text{Ar}]$     | 3                  | $\sqrt{15}$ BM  |
| $R : [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$               | 26               | + 2  | $[\text{Ar}]3d^6$ | 4                  | $\sqrt{24}$ BM  |

Thus, order of spin-only magnetic moment =  $Q < R < P$

13. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is(are)

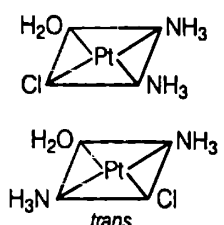
[JEE Advanced 2013, More than One Option]

- (a)  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$   
(b)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  and  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+$   
(c)  $[\text{CoBr}_2\text{Cl}_2]^{2-}$  and  $[\text{PtBr}_2\text{Cl}_2]^{2-}$   
(d)  $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{Cl}$  and  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$

Ans. (b, d) Depending on the structure of the complex, different types of isomerism are shown.

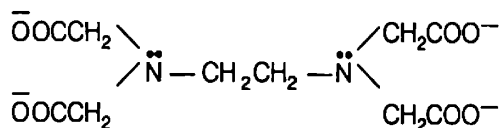
| Complex                                                                                                  | Isomerism                                  |
|----------------------------------------------------------------------------------------------------------|--------------------------------------------|
| A. $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$<br>$(\text{C}_2(\text{NH}_3)_4\text{Cl}_2)\text{Cl}$ | Neither of structural nor stereo isomerism |
| B. $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$                                                             | <p>trans w.r.t. Cl<br/>cis w.r.t. Cl</p>   |



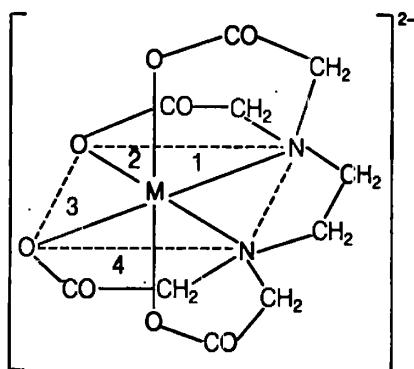
| Complex                                                                   | Isomerism                                                                                                           |
|---------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|
| $[\text{Pt}(\text{H}_2\text{O})(\text{NH}_3)_2\text{Cl}]^+$               |                                    |
| C. $[\text{CoBr}_2\text{Cl}_2]^{2-}$<br>$[\text{PtBr}_2\text{Cl}_2]^{2-}$ | $sp^3$ tetrahedral<br>$dsp^2$ -square planar                                                                        |
| D. $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{Cl}$                     | $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{Cl}$<br>$[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{NO}_3$ } ionisation |
| $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$                            | $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$<br>$[\text{Pt}(\text{NH}_3)_3\text{Br}]\text{Cl}$ } ionisation       |

14. EDTA<sup>4-</sup> is ethylenediaminetetraacetate ion. The total number of N—Co—O bond angles in  $[\text{Co}(\text{EDTA})]^-$  complex ion is [JEE Advanced 2013, Integer Type]

Ans. (8) EDTA is a multidentate ligand as it can donate six pairs of electrons – two pair from the two nitrogen atoms and four pair from the four terminal oxygens of the —COO<sup>-</sup> groups.



The structure of a chelate of a divalent Co<sup>2+</sup> with EDTA is shown as



Each N has four N—Co—O bonds thus total eight N—Co—O bonds.

15. As per IUPAC nomenclature, the name of the complex  $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$  is [JEE Advanced 2012, Single Option]

- (a) tetraaquadiamminecobalt (III) chloride  
(b) tetraaquadiamminecobalt (III) chloride  
(c) diaminetetraaquacobalt (III) chloride  
(d) diamminetetraaquacobalt (III) chloride

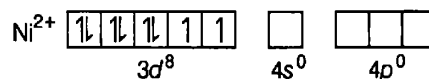
Ans. (d) First of all, the compound has complex positive part  $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{3+}$  therefore, according to IUPAC conventions, positive part will be named first. Secondly, in writing name of complex, ligands are named first in alphabetical order, irrespective of its charge, hence "ammine" will be written prior to "aqua".

16.  $\text{NiCl}_2[\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)]_2$  exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic) the coordination geometries of Ni<sup>2+</sup> in the paramagnetic and diamagnetic states are respectively

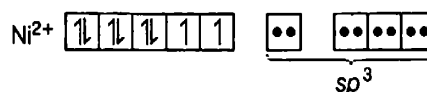
[JEE Advanced 2012, Single Option]

- (a) tetrahedral and tetrahedral  
(b) square planar and square planar  
(c) tetrahedral and square planar  
(d) square planar and tetrahedral

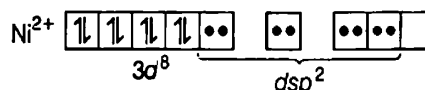
Ans. (c) In the given complex,  $\text{NiCl}_2[\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)]_2$  nickel is in +2 oxidation state and the ground state electronic configuration of Ni<sup>2+</sup> ion in free gaseous state is



For the given four-coordinated complex to be paramagnetic, it must possess unpaired electrons in the valence shell. To satisfy this condition, four lone pairs from the four ligands occupies the four  $sp^3$  hybrid orbitals as :



Therefore, geometry of paramagnetic complex must be tetrahedral. On the other hand, for complex to be diamagnetic, there should not be any unpaired electrons in the valence shell. This condition can be fulfilled by pairing electrons of 3d orbitals against Hund's Rule as



The above electronic arrangement gives  $dsp^2$  hybridisation and therefore, square planar geometry to the complex.

17. Geometrical shapes of the complexes formed by the reaction of Ni<sup>2+</sup> with Cl<sup>-</sup>, CN<sup>-</sup> and H<sub>2</sub>O, respectively, are

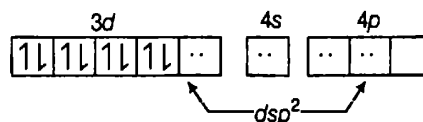
- (a) octahedral, tetrahedral and square planar

[IIT JEE 2011, Single Option]

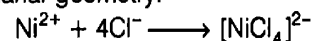
- (b) tetrahedral, square planar and octahedral  
(c) square planar, tetrahedral and octahedral  
(d) octahedral, square planar and octahedral

Ans. (b)  $\text{Ni}^{2+} + 4\text{CN}^- \rightarrow [\text{Ni}(\text{CN})_4]^{2-}$

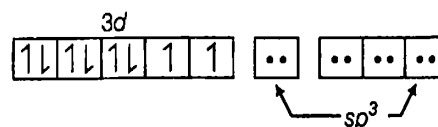
Here Ni<sup>2+</sup> has  $d^8$ -configuration with CN<sup>-</sup> as strong ligand.



$d^8$ -configuration in strong ligand field gives  $dsp^2$  hybridisation, hence square planar geometry.

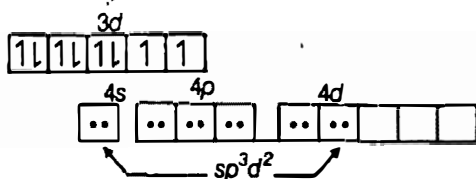


Here Ni<sup>2+</sup> has  $d^8$ -configuration with Cl<sup>-</sup> as weak ligand.



$d^8$ -configuration in weak ligand field gives  $sp^3$  hybridisation, hence tetrahedral geometry.

$Ni^{2+}$  with  $H_2O$  forms  $[Ni(H_2O)_6]^{2+}$  complex and  $H_2O$  is a weak ligand.



Therefore,  $[Ni(H_2O)_6]^{2+}$  has octahedral geometry.

18. Among the following complexes ( $K-P$ ),

$K_3[Fe(CN)_6]$  ( $K$ ),  $[Co(NH_3)_6]Cl_3$  ( $L$ ),  $Na_3[Co(ox)_3]$  ( $M$ ),

$[Ni(H_2O)_6]Cl_2$  ( $N$ ),  $K_2[Pt(CN)_4](O)$

and  $[Zn(H_2O)_6](NO_3)_2$  ( $P$ ) the diamagnetic complexes are

[IIT JEE 2011, Single Option]

(a)  $K, L, M, N$

(b)  $K, M, O, P$

(c)  $L, M, O, P$  (d)  $L, M, N, O$

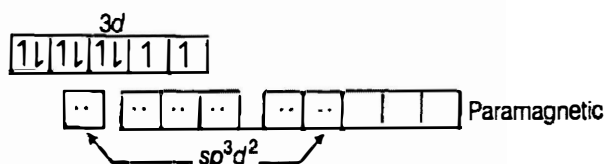
Ans. (c) For a diamagnetic complex, there should not be any unpaired electron in the valence shell of central metal.

In  $K_3[Fe(CN)_6]$ , Fe (III) has  $d^5$ -configuration (odd electrons), hence it is paramagnetic.

In  $[Co(NH_3)_6]Cl_3$ , Co (III) has  $d^6$ -configuration in a strong ligand field, hence all the electrons are paired and the complex is diamagnetic.

In  $Na_3[Co(ox)_3]$ , Co (III) has  $d^6$ -configuration and oxalate being a chelating ligand, very strong ligand and all the six electrons remains paired in lower  $t_{2g}$  level, diamagnetic.

In  $[Ni(H_2O)_6]Cl_2$ , Ni (II) has  $3d^8$ -configuration and  $H_2O$  is a weak ligand hence



In  $K_2[Pt(CN)_4]$ , Pt(II) has  $d^8$ -configuration and  $CN^-$  is a strong ligand, hence all the eight electrons are spin-paired. Therefore, complex is diamagnetic.

In  $[Zn(H_2O)_6](NO_3)_2$ , Zn (II) has  $3d^{10}$  configuration with all the ten electrons spin paired, hence diamagnetic.

19. The ionisation isomer of  $[Cr(H_2O)_4Cl(NO_2)]Cl$  is

[IIT JEE 2010, Single Option]

(a)  $[Cr(H_2O)_4(O_2N)]Cl_2$

(b)  $[Cr(H_2O)_4Cl_2](NO_2)$

(c)  $[Cr(H_2O)_4Cl(ONO)]Cl$

(d)  $[Cr(H_2O)_4Cl_2(NO_2)] \cdot H_2O$

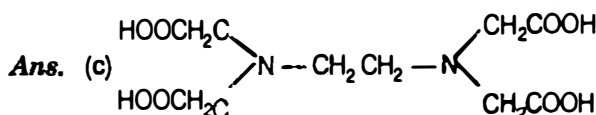
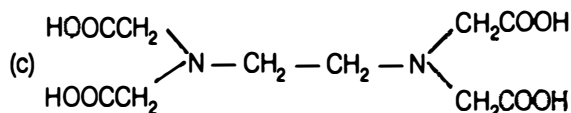
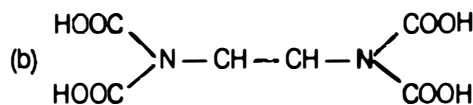
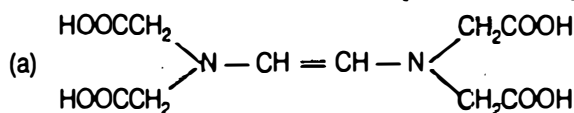
Ans. (b) Ionisation isomers are the complexes that produces different ions in solution, i.e., they have ions interchanged inside and outside the coordination sphere.

$[Cr(H_2O)_4Cl(NO_2)]Cl$  and  $[Cr(H_2O)_4Cl_2](NO_2)$  have different ions inside and outside the coordinate sphere and they are isomers.

Therefore, they are ionisation isomers.

20. The correct structure of ethylenediaminetetraacetic acid (EDTA) is

[IIT JEE 2010, Single Option]



21. The complex showing a spin-only magnetic moment of 2.82 BM is

[IIT JEE 2010, Single Option]

(a)  $Ni(CO)_4$

(b)  $[NiCl_4]^{2-}$

(c)  $Ni(PPh_3)_4$

(d)  $[Ni(CN)_4]^{2-}$

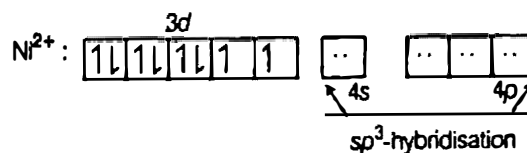
Ans. (b) Magnetic moment = 2.83 BM indicates that there are two unpaired electrons.

$$\mu = \sqrt{n(n+2)} \text{ BM}$$

$$= \sqrt{8} \text{ BM}$$

$$= 2.82 \text{ BM}$$

In  $[NiCl_4]^{2-}$ , Ni has  $d^8$  configuration and  $Cl^-$  is a weak ligand :



22. The octahedral complex of a metal ion  $M^{3+}$  with four monodentate ligands  $L_1, L_2, L_3$  and  $L_4$  absorb wavelengths in the region of red, green, yellow and blue respectively. The increasing order of ligand strength of the four ligands is

[JEE Main 2014]

(a)  $L_4 < L_3 < L_2 < L_1$

(b)  $L_1 < L_3 < L_2 < L_4$

(c)  $L_3 < L_2 < L_4 < L_1$

(d)  $L_1 < L_2 < L_4 < L_3$

Ans. (b) Ligand field strength  $\propto$  energy of light absorbed  $\propto 1/\text{wavelength of light absorbed}$ .

| $\lambda$      | $L_1$ | $L_2$ | $L_3$  | $L_4$ |
|----------------|-------|-------|--------|-------|
| Absorbed light | red   | green | yellow | blue  |

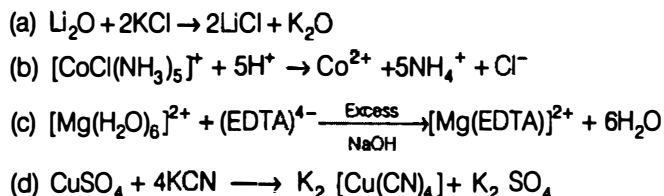
Wavelength of absorbed light decreases.

Increasing order of energy of wavelengths absorbed reflect greater extent of crystal field splitting. Hence, higher field strength of the ligand.

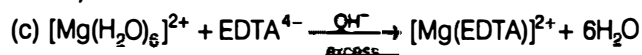
Energy: blue ( $L_4$ ) > green ( $L_2$ ) > yellow ( $L_3$ ) > red ( $L_1$ )

$\therefore L_4 > L_2 > L_3 > L_1 \rightarrow$  decreasing field strength of ligands.

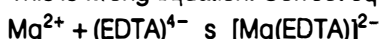
23. The equation which is balanced and represents the correct product (s) is [JEE Main 2014]



**Ans. (b)** (a)  $\text{Li}_2\text{O} + \text{KCl} \rightarrow 2\text{LiCl} + \text{K}_2\text{O}$  (wrong equation because a stronger base  $\text{K}_2\text{O}$  cannot be generated by a weaker base)  
 (b)  $[\text{CoCl}(\text{NH}_3)_5]^{+} + 5\text{H}^{+} \rightarrow \text{Co}^{2+}(\text{aq}) + 5\text{NH}_4^{+} + \text{Cl}^{-}$  (This is correct, all ammine complexes can be destroyed by adding  $\text{H}^{+}$ )



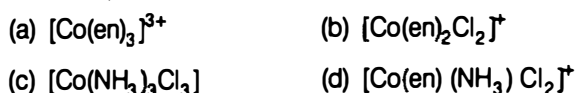
This is wrong equation. Correct equation is



(d) The given reaction is incorrect. It can be correctly represented as

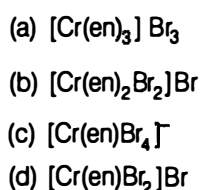


24. Which of the following complex species is not expected to exhibit optical isomerism? [JEE Main 2013]



**Ans. (c)** Optical isomerism is exhibited by only those complexes which lack elements of symmetry.  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  shows facial as well as meridional isomerism. But both forms contain a plane of symmetry. Thus, this complex does not exhibit optical isomerism.

25. Which among the following will be named as dibromidobis(ethylenediamine) chromium (III) bromide? [AIEEE 2012]



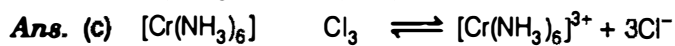
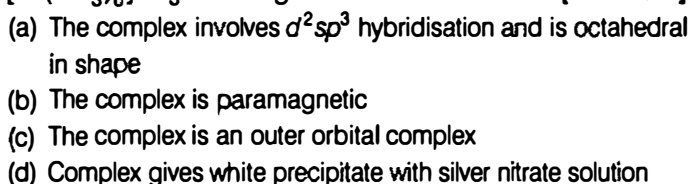
**Ans. (b)** Two Br, two (en) and one Cr are parts of complex. Charge on the complex is

$$\left. \begin{array}{l} 2(\text{Br}) = -2 \\ 2(\text{en}) = 0 \\ 1(\text{Cr}) = +3 \end{array} \right\} = +1$$

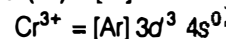
Thus, complex ion is  $[\text{Cr}(\text{en})_2\text{Br}_2]^{+}$

Since, anion is bromide thus, complex is  $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}$ .

26. Which of the following facts about the complex  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  is wrong? [AIEEE 2011]



Coordinate sphere    Ionisable



 Indicates lone pair of  $\text{NH}_3$  donated to Cr.

- (a)  $d^2sp^3$ -hybridisation, octahedral. Thus, correct.  
 (b) There are three unpaired electrons, hence paramagnetic. Thus, correct.  
 (c)  $d^2sp^3$ -inner orbital complex, thus statement (c) is incorrect.  
 (d) Due to ionisable  $\text{Cl}^{-}$  ions, white precipitate with  $\text{AgNO}_3$ , thus correct.

27. The magnetic moment (spin only) of  $[\text{NiCl}_4]^{2-}$  is [AIEEE 2011]

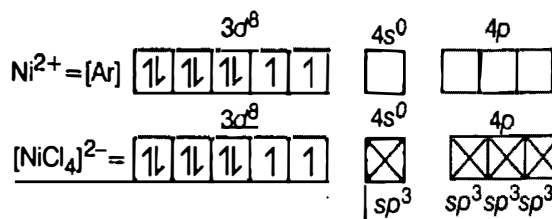
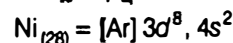
- (a) 1.82 BM (b) 5.46 BM  
 (c) 2.82 BM (d) 1.41 BM

**Ans. (c)**  $[\text{NiCl}_4]^{2-}$ ; oxidation number of

$\text{Ni}, x - 4 = -2$

$\therefore$

$x = +2$



Four  $sp^3$ -hybrid orbitals tetrahedral

$\text{Cl}^{-}$  is a weak ligand and thus unpaired electrons are not paired.  
 Magnetic moment (spin only)

$= \sqrt{n(n+2)} \text{ BM}$

$= \sqrt{2(2+2)} \text{ BM}$

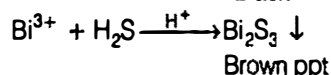
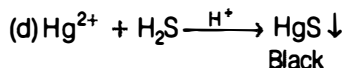
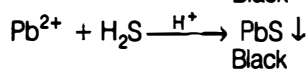
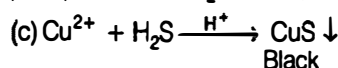
$= \sqrt{8} = 2.828 \text{ BM}$

## 19. Salt Analysis

1. The pair(s) of ions where both the ions are precipitated upon passing  $\text{H}_2\text{S}$  gas in the presence of dilute  $\text{HCl}$ , is (are) [JEE Advanced 2015, Single Option]

- (a)  $\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$  (b)  $\text{Bi}^{3+}$ ,  $\text{Fe}^{3+}$   
 (c)  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  (d)  $\text{Hg}^{2+}$ ,  $\text{Bi}^{3+}$

**Ans. (d)** Only radicals of I and II group of qualitative analysis get precipitated with  $\text{H}_2\text{S}$  in the presence of dilute  $\text{HCl}$ .



$\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  are not precipitated as sulphide.

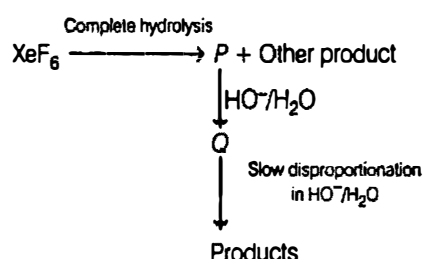
## 20. Group 18 [VIIIA - The Noble Gases]

1. Which one has the highest boiling point? [JEE Main 2015]

- (a) He  
(b) Ne  
(c) Kr  
(d) Xe

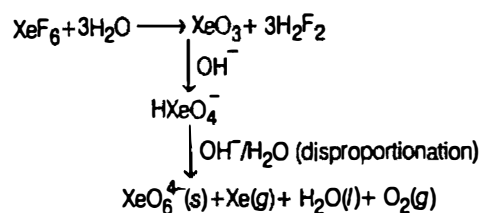
**Ans. (d)** As we move down the group of noble gases, molecular mass increases by which dipole produced for a moment and hence London forces increases from He to Xe. Therefore more amount of energy is required to break these forces, thus boiling point also increases from He to Xe.

2. Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is [JEE Advanced 2014, Single Option]



- (a) 0  
(b) 1  
(c) 2  
(d) 3

**Ans. (c)**  $\text{XeF}_6$  on complete hydrolysis produces  $\text{XeO}_3$ .



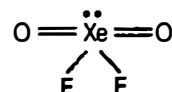
Thus, (c) is the correct answer.

3. The shape of  $\text{XeO}_2\text{F}_2$  molecule is

[JEE Advanced 2012, Single Option]

- (a) trigonal bipyramidal (b) square planar  
(c) tetrahedral (d) see-saw

**Ans. (d)** In  $\text{XeO}_2\text{F}_2$ , the bonding arrangement around the central atom Xe is



$$4\sigma \text{ bonds} + 1.0 \text{lp} = 5$$

$\Rightarrow$  Hybridization of Xe =  $sp^3d$

$sp^3d$  hybridization corresponds to trigonal bipyramidal geometry.

Also, in trigonal bipyramidal geometry, lone pairs remain present on equatorial positions in order to give less electronic repulsion.

